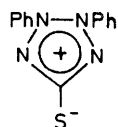


Cycloaddition Reactions of Dehydrodithizone. X-Ray Crystal Structures of 5-Diethylamino-4-methyl-1-phenyl-3-phenylazopyrazole, 4a,5,6,7,8,8a-Hexahydro-6-methyl-8a-morpholino-1-phenyl-3-phenylazo-1*H*-pyrido-[4,3-*e*][1,3,4]thiadiazine, and 3'-Phenyl-5'-phenylazo-2-pyrrolidino-spiro-[1*H*-indene-1,2' (3' *H*)-[1,3,4]thiadiazole]¹

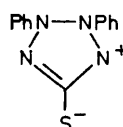
By Gerhard V. Boyd* and Timothy Norris, Department of Chemistry, Chelsea College, London SW3 6LX
Peter F. Lindley,* Department of Crystallography, Birkbeck College, London WC1

The title compounds [(3a), (11), and (15a)] were obtained from dehydrodithizone and, respectively, 1-diethylaminopropyne, the morpholine enamine of 1-methyl-4-piperidone, and 2-pyrrolidinoindene, and their structures were determined by single-crystal X-ray structure analysis. Likewise, reaction of dehydrodithizone with 1-dimethylamino-2-phenylacetylene gave the phenylazopyrazole (3c), with β -piperidinostyrene the phenylazo-1,3,4-thiadiazine (12), and with 2-piperidino- and 2-morpholino-indene the phenylazospiro[indene-[1,3,4]thiadiazoles] (15b and c). In contrast, dimethyl acetylenedicarboxylate and tetraphenylcyclopentadienone formed 1,3-dipolar cycloadducts, which are formulated as the thiazolo[3,2-*d*]tetrazoles (4) and (5) [or (6)], respectively. The different modes of behaviour of dehydrodithizone towards electron-rich and electron-poor components are rationalized by means of frontier-orbital theory.

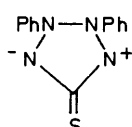
MESOIONIC compounds containing a five-membered ring may be divided into two classes, in which the heteroatoms contributing two π -electrons are, respectively, adjacent and non-adjacent. The most interesting aspect of the chemistry of the latter is the variety of cycloaddition reactions they undergo. Ever since the discovery² of the reaction of unsaturated esters and nitriles with sydrones and Huisgen's fundamental work,³ which demonstrated that cycloadditions of these systems represented a special case of 1,3-dipolar cycloadditions, there has been a constant stream of reports in this field, which shows no sign of abating.⁴ In contrast, mesoionic compounds in the first class, of which only a few are known, are reluctant to form cycloadducts with the usual dipolarophiles.⁵ Dehydrodithizone (1) alone has been reported (by Rajagopalan and Penev⁶) to undergo such reactions with dimethyl acetylenedicarboxylate, tetracyanoethylene, and enamines. These authors



(1)



(1a)



(1b)

pointed out that dehydrodithizone, unlike members of the sydnone class, contained a unique cross-conjugated system [see (1a)] and deduced the gross structure and orientation of their products by reference to this canonical

¹ Preliminary reports, G. V. Boyd, T. Norris, and P. F. Lindley, *J.C.S. Chem. Comm.*, 1974, 639; 1975, 100.

² V. F. Vasileva, V. G. Yashunskii, and M. N. Shchukina, *Zhur. obshchei Khim.*, 1960, **30**, 698.

³ (a) R. Huisgen, *Angew. Chem. Internat. Edn.*, 1963, **2**, 565; (b) R. Huisgen, in 'Aromaticity,' Chem. Soc. Special Publ. No. 21, 1967, p. 51.

form, others, *e.g.* (1b), being 'inconsequential'. In the course of our work⁵ on mesoionic systems of the first kind we investigated the reactions of dehydrodithizone with various olefins and acetylenes and found several cases which did not conform to the pattern suggested by Rajagopalan and Penev.

Our first cycloaddition experiment concerned the reaction of dehydrodithizone with the electron-rich dipolarophile, 1-diethylaminopropyne. We obtained a mixture of two orange compounds in the ratio 7 : 1, whose electronic and i.r. spectra were almost identical. The n.m.r. spectrum of each contained signals due to two *N*-phenyl groups, a methyl group, and a diethylamino-substituent. Neither was the expected cycloadduct (2), since mass spectrometry indicated that each had the composition of a 1 : 1 adduct minus sulphur. Reduction of the major isomer with tin(II) chloride-hydrochloric acid gave aniline and another primary amine, C₁₄H₂₀N₄, characterized as its *p*-tolylsulphonyl derivative. The compound therefore possessed a phenylazo-substituent and we considered that this was probably attached to a pyrazole nucleus; this yields two possible structures (3a and b). An X-ray crystal structure determination (see below) of the major isomer showed that it was (3a); the minor product, because of its close similarity, is assigned structure (3b). The action of 1-dimethylamino-2-phenylacetylene on dehydrodithizone likewise led to a

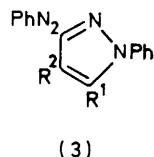
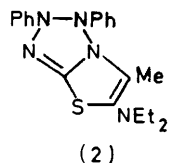
⁴ Recent articles include (a) H. Matsukubo and H. Kato, *J.C.S. Perkin I*, 1975, 632; (b) T. Ibata, M. Hamaguchi, and H. Kiyohara, *Chem. Letters*, 1975, 21; (c) K. T. Potts, J. Baum, and E. Houghton, *J. Org. Chem.*, 1974, **39**, 3631; (d) S. Nakazawa, T. Kiyosawa, K. Hirakawa, and H. Kato, *J.C.S. Chem. Comm.*, 1974, 621; (e) A. R. McCarthy, W. D. Ollis, and C. A. Ramsden, *J.C.S. Perkin I*, 1974, 624.

⁵ G. V. Boyd and T. Norris, *J.C.S. Perkin I*, 1974, 1028.

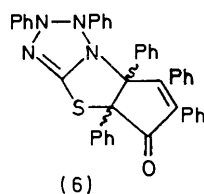
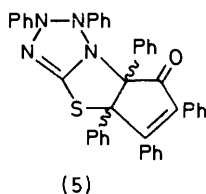
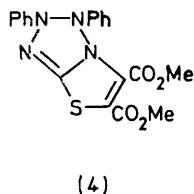
⁶ P. Rajagopalan and P. Penev, *Chem. Comm.*, 1971, 490.

sulphur-free compound, which we formulate as either (3c) or, less probably, (3d).

The unexpected course of the reaction with the ynamines prompted us to study other cycloadditions of dehydrodithizone, including some reported by the American authors.⁶ Dimethyl acetylenedicarboxylate gave an adduct whose i.r. and n.m.r. spectra were consistent with the proposed⁶ structure (4). Significantly, the mass spectrum of the product, like that of dehydrodithizone itself, contained a signal at m/e 182, which we assign to the azobenzene ion. The same type of cycloadduct was formed by reaction with tetraphenylcyclopentadienone. We had thought that this might function as a 4π -component, yielding a new kind of product or a compound derived therefrom, but the spectral characteristics of the isolated adduct, in particular, cyclopent-2-enone carbonyl absorption at 1715 cm^{-1} and the appearance of the azobenzene fragment signal in the mass spectrum, indicated that it had the gross constitution (5) or (6) and that it originated by addition of dehydrodithizone to one of the electron-deficient double bonds of



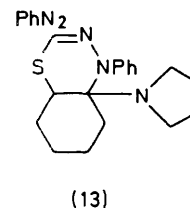
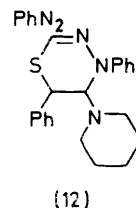
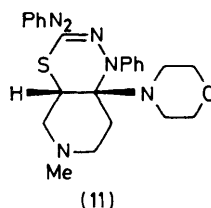
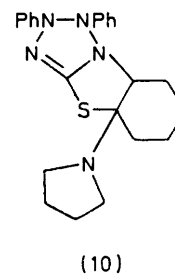
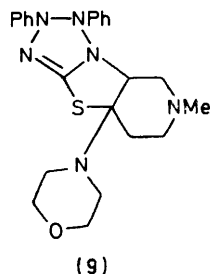
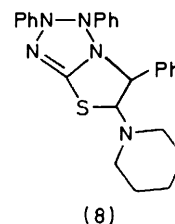
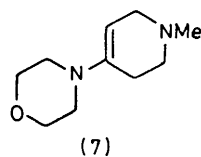
- a ; $R^1 = \text{NEt}_2$, $R^2 = \text{Me}$
 b ; $R^1 = \text{Me}$, $R^2 = \text{NEt}_2$
 c ; $R^1 = \text{NMe}_2$, $R^2 = \text{Ph}$
 d ; $R^1 = \text{Ph}$, $R^2 = \text{NMe}_2$



tetraphenylcyclopentadienone. The precise orientation and configuration of this cycloadduct and those of a minor product are at present under investigation.

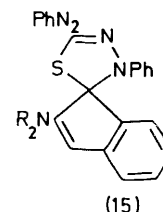
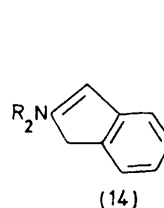
We next studied the reactions of dehydrodithizone with enamines, representative of electron-rich olefins. The additions to β -piperidinostyrene, 1,2,5,6-tetrahydro-1-methyl-4-morpholinopyridine (7), and pyrrolidinocyclohexene are claimed⁶ to lead to analogues of (4), *i.e.* the 1,3-dipolar cycloadducts (8)—(10), respectively. On repeating this work, using the first two enamines, we obtained products whose properties were in substantial agreement with the published data and further details kindly supplied by Dr. Rajagopalan. However, the proposed structures are untenable in view of the mass spectra of the two adducts, neither of which contained the crucial peak due to the azobenzene radical ion. The compound obtained from the morpholino-enamine (7) was suitable for *X*-ray analysis, which established for it

the 1,3,4-thiadiazine structure (11), the most notable feature being the *cis*-fusion of the rings. The other



enamine adducts are accordingly most likely the analogues (12) and (13).

Yet another type of compound was formed in the reaction of dehydrodithizone with enamines derived from indan-2-one, namely 2-pyrrolidino-, 2-piperidino-, and 2-morpholino-indene (14a—c). The three red crystalline products had virtually identical electronic spectra, their mass spectra indicated the composition of 1:1 adducts minus two atoms of hydrogen and lacked the azobenzene signal, and their n.m.r. spectra contained only resonances due to aromatic protons, the amine grouping, and one uncoupled olefinic proton. The structure of the



- a ; $\text{NR}_2 = \text{pyrrolidino}$
 b ; $\text{NR}_2 = \text{piperidino}$
 c ; $\text{NR}_2 = \text{morpholino}$

pyrrolidino-derivative was elucidated by *X*-ray crystallography and shown to be (15a). Consequently, the other dehydro-adducts are formulated as (15b and c).

Discussion.—It emerges that dehydrodithizone undergoes different kinds of reaction with olefins and acetylenes, depending on whether the multiple bond is electron-poor or electron-rich. Reagents in the former category yield 1,3-cycloadducts, whereas the others give products which do not contain a tetrazole ring. The contrasting behaviour of the two types can be rationalized by means of frontier-orbital theory,⁷ which has been applied to diverse cycloaddition reactions.⁸ Figure 1 lists the energies of the highest occupied (HOMO) and lowest unoccupied (LUMO) molecular orbitals of dehydrodithizone and the associated atomic orbital coefficients, together with those of acrylaldehyde and dimethylaminoethylene, simple representatives of, respectively, electron-poor and electron-rich olefins.* It is seen that

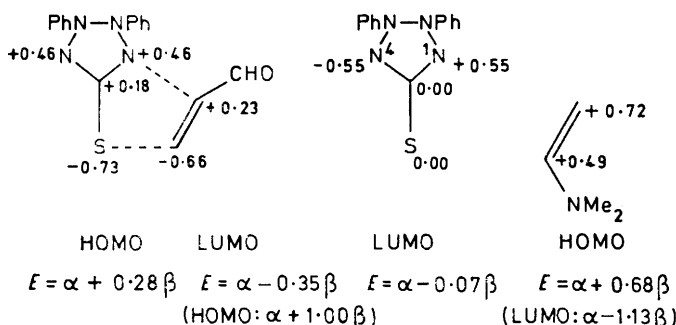


FIGURE 1 Energy levels and atomic orbital coefficients of dehydrodithizone, acrylaldehyde, and dimethylaminoethylene

the reaction with acrylaldehyde is dominated by interaction of the HOMO of dehydrodithizone with the LUMO of acrylaldehyde rather than the reverse, since in the former case the difference in energies is less. These MOs also possess suitable symmetry because their atomic orbital coefficients have the right signs for formation of the transition state leading to a 1,3-cycloadduct with the orientation indicated. In the case of the reaction with dimethylaminoethylene, on the other hand, the theory requires that the HOMO of the olefin and the LUMO of dehydrodithizone interact most strongly and, as the latter has a node passing through the sulphur and carbon atoms, bonding to the sulphur atom does not occur. Furthermore, addition to N-1 and N-4 is forbidden on grounds of symmetry. Concerted cycloaddition therefore does not take place as it would have to pass through a transition state of high energy and other modes of reaction intervene.

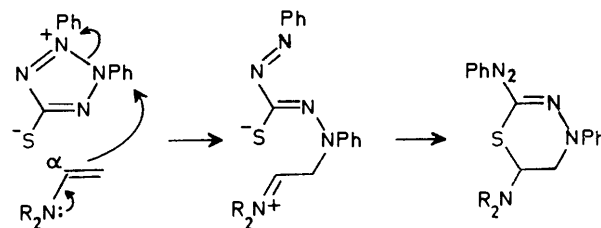
It is evident that these other modes involve opening of the tetrazole ring and the question arises as to whether this precedes attack by the nucleophilic reagent or is

* These results were obtained by the simple Hückel method, by employing the following parameters: $h_S = 0.3$, $h_N = 0.5$, $h_{NMe} = h_{NPh} = 1.5$, $h_O = 1$; $k_{CS} = k_{CO} = 1$, $k_{CN} = 0.8$, $k_{NN} = 0.7$. The arguments that follow do not depend on the particular choice of parameters, since the ordering of energy levels and the symmetry of the molecular orbitals are not affected by it.

⁷ K. Fukui, 'Theory of Orientation and Stereoselection,' Springer-Verlag, Heidelberg, 1970.

⁸ For a recent account and leading references, see K.-L. Mok and M. J. Nye, *J.C.S. Perkin I*, 1975, 1810.

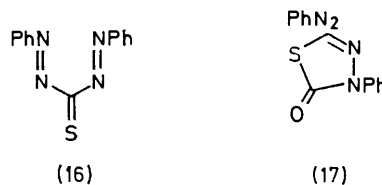
concomitant with it. We favour the former alternative, chiefly because of the orientation of the morpholino-substituent in the adduct (11). Fission of the tetrazolium ring caused by approach of the enamine (see Scheme 1) requires that in the product the sulphur atom



SCHEME 1

is bonded to C_α of the olefin, whereas it is actually attached to the other carbon atom. The first possibility, prior ring-opening, yields the valence isomer (16). This is the structure originally assigned⁹ to the mesoionic compound, but later disputed¹⁰ on chemical grounds and finally disproved¹¹ by X-ray analysis. An attempt¹² to prepare it by rearrangement of dehydrodithizone led instead to a derivative of 1,3,4-benzothiadiazine.¹³ Nonetheless, it appears to us that the formation¹⁴ of the 1,3,4-thiadiazolinone (17) by the action of pentacarbonyliron on dehydrodithizone may involve the valence isomer and we propose it as an intermediate in the reactions with ynamines and enamines.

Cycloaddition of diethylaminopropene to the 1,3-diene system in (16a), the *cisoid* conformer of (16), would yield the thiadiazine (18), which can undergo disrotatory cyclisation to the ylide (19). Loss of sulphur leads to the product (3a) (Scheme 2). Addition of the ynamine in the opposite sense produces the minor isomer (3b); the



process corresponding to that outlined in Scheme 1 would give solely this isomer. The sequence (18) → (3a) is analogous to the formation¹⁵ of pyrazoles from 6*H*-1,3,4-thiadiazines, which involves the intermediacy of the unstable 4*H*-tautomers.¹⁶ In the reaction of dehydrodithizone with enamines, the Diels-Alder products, *e.g.* (11), cannot extrude sulphur and the process

⁹ E. Fischer and A. Besthorn, *Annalen*, 1882, **212**, 316.

¹⁰ E. Bamberger, R. Padova, and E. Ormerod, *Annalen*, 1926, **446**, 260.

¹¹ Q. Fernando and Y. Kushi, *Chem. Comm.*, 1969, 1240; *J. Amer. Chem. Soc.*, 1970, **92**, 1965.

¹² J. W. Ogilvie and A. H. Corwin, *J. Amer. Chem. Soc.*, 1961, **83**, 5023.

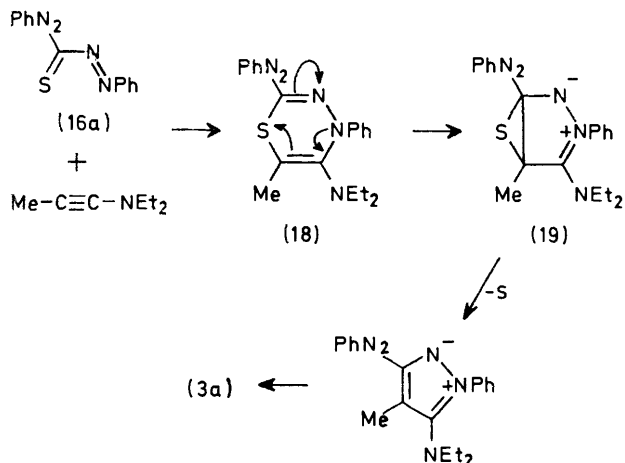
¹³ W. S. McDonald, H. N. M. H. Irving, G. Raper, and D. C. Rupainwar, *Chem. Comm.*, 1969, 392.

¹⁴ P. N. Preston, N. J. Robinson, K. Turnbull, and T. J. King, *J.C.S. Chem. Comm.*, 1974, 998.

¹⁵ H. Beyer, H. Honeck, and L. Reichelt, *Annalen*, 1970, **741**, 45.

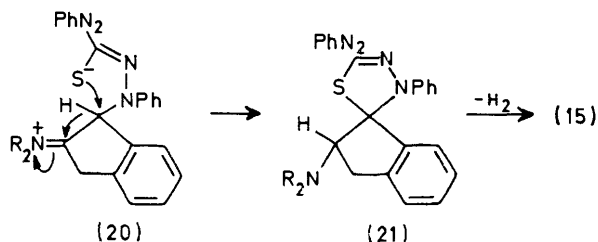
¹⁶ R. R. Schmidt, *Angew. Chem. Internat. Edn.*, 1975, **14**, 581.

consequently terminates at this stage. The *cis*-configuration of compound (11) suggests that the cycloaddition may be concerted, a further argument against



SCHEME 2

the mechanism of Scheme 1. However, the spiro-compounds obtained from indanone enamines could arise in this way. The dipolar intermediates (20) can undergo concerted ring-closure and [1,2] hydride shift to



give (21), which then lose hydrogen to yield the more highly conjugated products (15). Alternatively, the acyclic valence tautomer (16) may be invoked to rationalize these reactions also, since polar addition of the

unequivocal explanation based on steric effects can be offered—careful examination of scale models has not yet revealed any obstruction to the formation of cycloadducts analogous to (11).

Description of the Structures (3a), (11), and (15a).—The crystal structures of 5-diethylamino-4-methyl-1-phenyl-3-phenylazopyrazole (3a) and 3'-phenyl-5'-phenylazo-2-pyrrolidinospiro-[1*H*-indene-1,2'(3'*H*)-[1,3,4]thiadiazole] (15a) consist of discrete molecules (Figures 2 and 3 respectively). The crystal structure of 4a,5,6,7,8,8a-hexahydro-6-methyl-8a-morpholino-1-phenyl-3-phenylazo-1*H*-pyrido[4,3-*e*][1,3,4]thiadiazine (11) is composed of an asymmetric unit containing two molecules which are chemically identical. Figure 4 (a and b) shows the asymmetric unit and also one of the individual molecules. The atom numbering schemes for the three structures together with appropriate intramolecular bond lengths and angles are shown schematically in Figures 5—7. Further details of the molecular geometries are given in Tables 7—9.

A feature common to all three structures is the presence of a *W*-shaped array of atoms which originates from the dehydrodithizone molecule. The array is defined by N(1), N(2), C(3), N(3), and N(4) in (3a), N(4), N(3), C(1), N(1), and N(2) in (15a), and N(4), N(3), C(2), N(11), and N(12) in (11), and contrasts sharply with the cyclic arrangement of these atoms in dehydrodithizone.¹¹ A similar *W*-shaped array has been found in the bicyclic oxidation product of dithizone.¹³

In (3a) the pyrazole ring is planar within experimental error. The phenylazo-unit does not lie precisely in this plane and is itself non-planar. These distortions can be described in terms of the torsion angles N(2)–C(3)–N(3)–N(4) (173.8°), indicating the displacement of N(4) out of the plane of the pyrazole ring (0.115 Å); C(3)–N(3)–N(4)–C(41) (178.9°), indicating the approximate planarity of the linking azo nitrogen atoms; and N(3)–N(4)–C(41)–C(46) (11.7°), indicating the twist of the phenyl ring with respect to the N(4)–C(41) bond; the dihedral

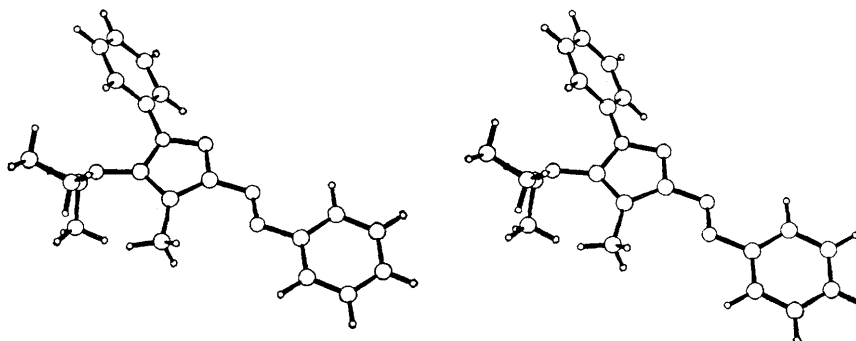


FIGURE 2 Stereodrawing of a molecule of 5-diethylamino-4-methyl-1-phenyl-3-phenylazopyrazole (3a)

indanone enamines would produce the same intermediates (20). The cause of the divergent behaviour of the indene compounds is not clear. Their electronic structure does not appear to differ fundamentally from that of simpler enamines, particularly β -piperidinostyrene, and no

angle between the least-squares planes through the phenyl ring and the pyrazole ring is 6.0°. The phenyl ring in the phenylazo-unit is planar but is asymmetrically disposed with respect to the N(4)–C(41) bond. The opening out of the N(4)–C(41)–C(46) angle to 124.0(4)°

and the twist of the phenyl ring with respect to the plane defined by N(3), N(4), C(41) may be due in part to steric hindrance between N(3) and H(46). The calculated N(3) \cdots H(46) separation (2.49 Å) is slightly less

but is twisted about the N(1)–C(11) bond to give a dihedral angle of 51.0° with the plane of the pyrazole ring. This rotation minimises the non-bonded repulsions between this ring and the diethylamino-unit.

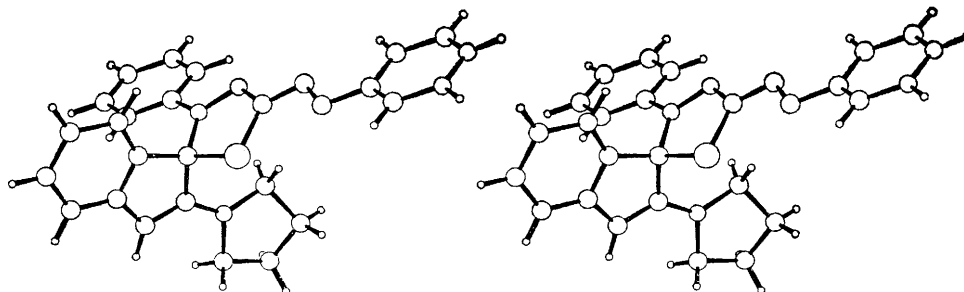


FIGURE 3 Stereodrawing of a molecule of 3'-phenyl-5'-phenylazo-2-pyrrolidinospiro-[1*H*-indene-1,2'(3'*H*)-[1,3,4]thiadiazole](15a)

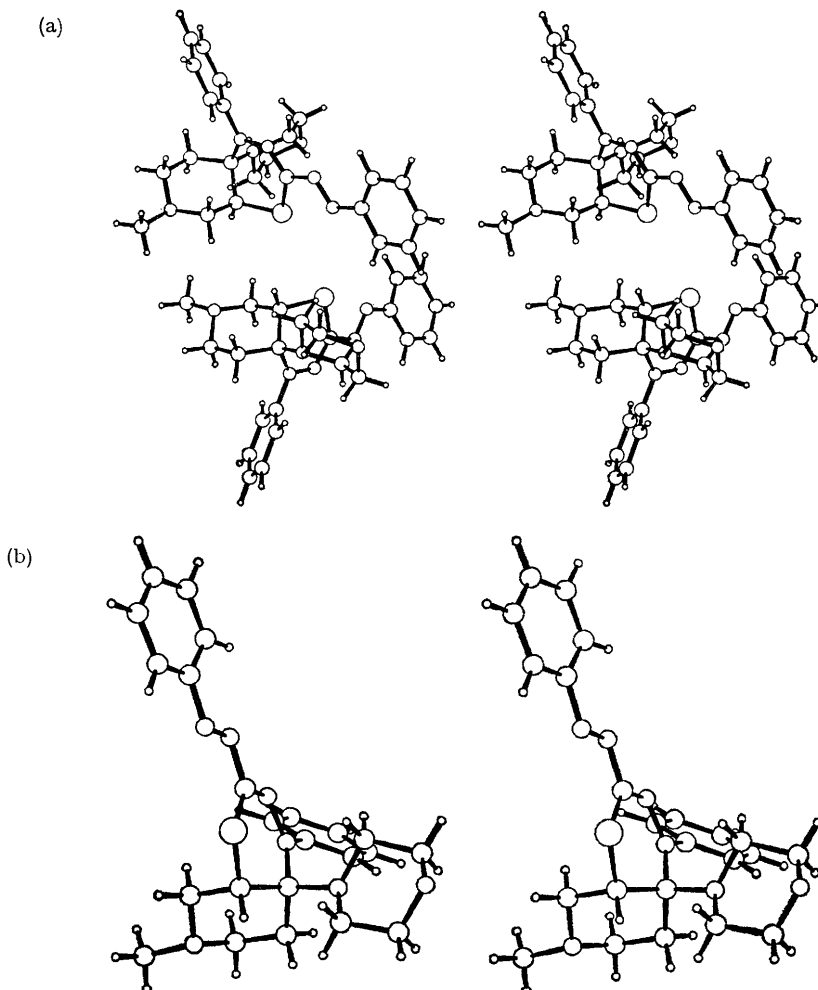


FIGURE 4 (a) Stereodrawing of the asymmetric unit of 4a,5,6,7,8,8a-hexahydro-6-methyl-8a-morpholino-1-phenyl-3-phenylazo-1*H*-pyrido[4,3-*e*][1,3,4]thiadiazine (11) viewed along the unit cell x axis; (b) stereodrawing of one molecule of the pyridothiadiazine (11)

than the sum of the respective van der Waals radii¹⁷ (2.70 Å).

The remaining phenyl ring, C(11)–16), is also planar

The diethylamino-unit is also rotated out of the plane of the pyrazole ring about the C(5)–N(5) bond; the dihedral angle between the least-squares plane defined by

the pyrazole ring and the plane through atoms C(5), C(51), and C(53) is 117.7° . This latter rotation minimises non-bonded contacts between the diethylamino-unit and the neighbouring phenyl ring at N(1) and the methyl group at C(4). The C(5)–N(5) bond length, $1.386(5)$ Å, however, lies approximately midway between the values (1.47 and 1.29 Å) expected for CN single and double bonds, respectively, suggesting some double-bond

character in this linkage. The geometry about N(5) is slightly flattened, with N(5) displaced by -0.23 Å out of the plane defined by C(5), C(51), and C(53); in (11) the displacements of N(25) out of the plane through C(5), C(26), and C(30) are 0.34 and 0.37 Å for the two molecules respectively.

In (15a) the thiadiazole ring is planar within experimental error. The S(1)–C(1) bond distance, $1.75(1)$ Å, is significantly less than the S(1)–C(2) distance, $1.84(1)$ Å, as would be expected for an interaction involving an sp^2 -hybridised carbon atom as opposed to one that is sp^3 -hybridised.

The phenylazo-unit is displaced out of the plane of the thiadiazole ring but in a slightly different way to that found in (3a). The relevant torsion angles are N(3)–C(1)–N(1)–N(2) (-179.6°), indicating the approximate

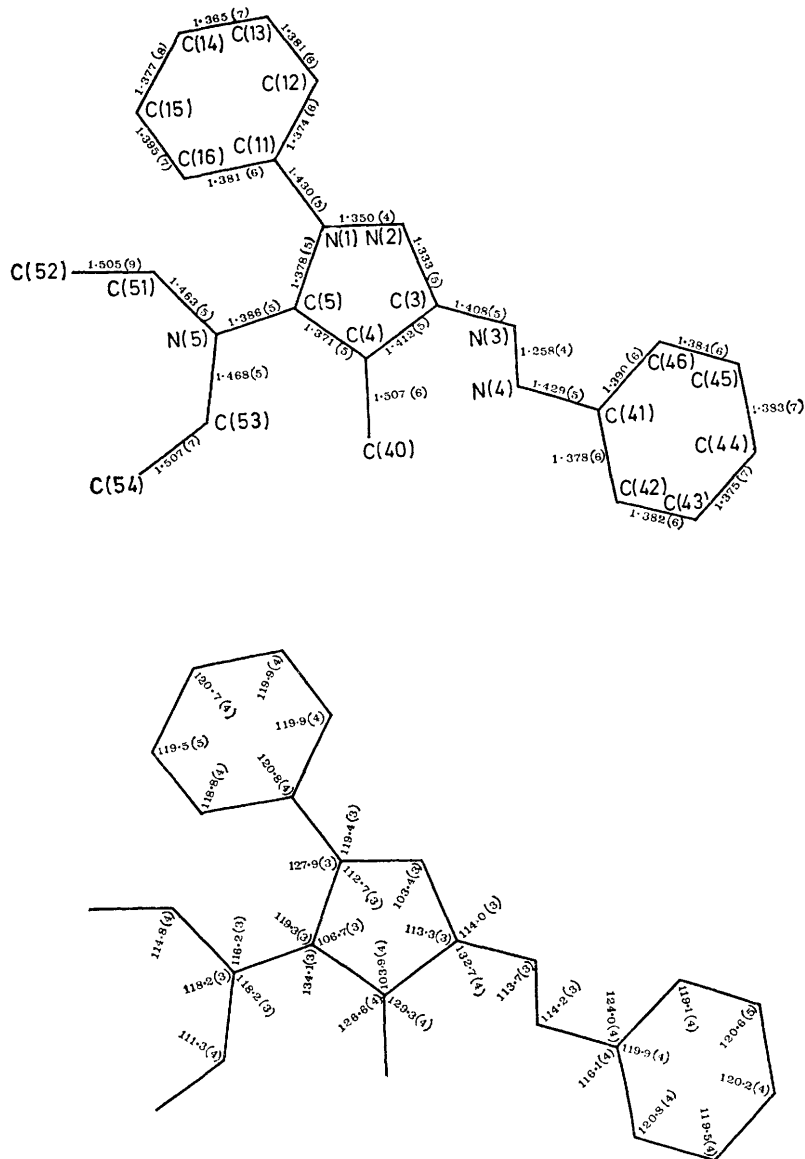


FIGURE 5 Schematic drawing of the molecule of 5-diethylamino-4-methyl-1-phenyl-3-phenylazopyrazole (3a) showing the labelling of the atoms and the bond lengths (Å) and bond angles ($^\circ$) (estimated standard deviations in parentheses)

character in this linkage. The geometry about N(5) is slightly flattened, with N(5) displaced by -0.23 Å out of the plane defined by C(5), C(51), and C(53); in (11) the displacements of N(25) out of the plane through C(5), C(26), and C(30) are 0.34 and 0.37 Å for the two molecules respectively.

In (15a) the thiadiazole ring is planar within experimental error. The S(1)–C(1) bond distance, $1.75(1)$ Å,

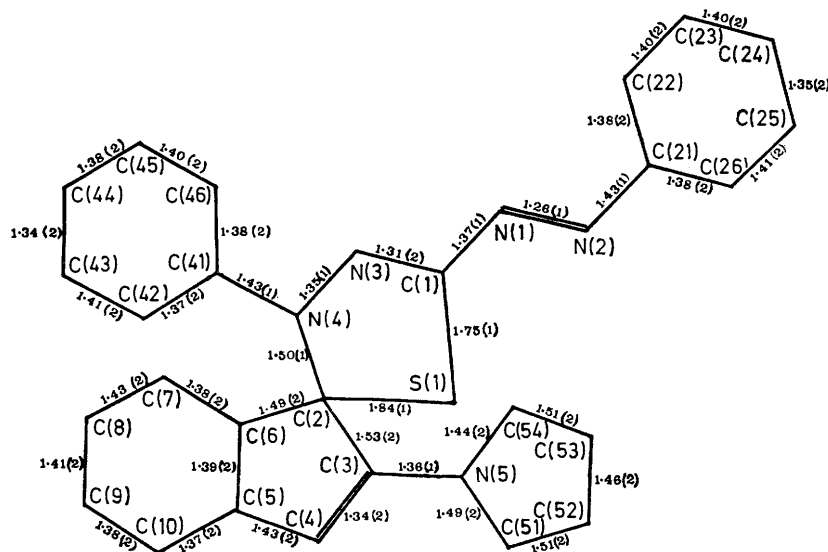
equal displacement of N(1) and N(2) out of the plane of the thiadiazole ring (0.050 and 0.045 Å, respectively); C(1)–N(1)–N(2)–C(21) (174.7°), indicating a rotation of the PhN: unit about the N(1)–N(2) bond; and N(1)–N(2)–C(21)–C(22) (-8.0°), indicating a twist of the planar phenyl ring about the N(2)–C(21) bond; the phenyl ring makes a dihedral angle of 14.4° with the thiadiazole ring. As in (3a), the N(2)–C(21)–C(22)

angle is opened out to $124(1)^\circ$; the calculated $N(2) \cdots H(22)$ separation is 2.71 \AA .

The $S(1)-N(1)$ separation, 2.79 \AA , is considerably less than the sum of the respective van der Waals radii¹⁷ (3.35 \AA), which may indicate some weak interaction between these two atoms.

least-squares planes defined by the indene unit and the thiaziazole ring is 90.5° .

The $C(3)-N(5)$ bond length, $1.36(1) \text{ \AA}$, is indicative of significant double-bond character. The atom $N(5)$ lies in the plane defined by $C(3)$, $C(51)$, and $C(54)$ and the dihedral angle between this plane and the plane defined



Angles not shown

in figure: $S(1)-C(2)-C(6) 110(1)$
 $N(4)-C(2)-C(3) 115(1)$

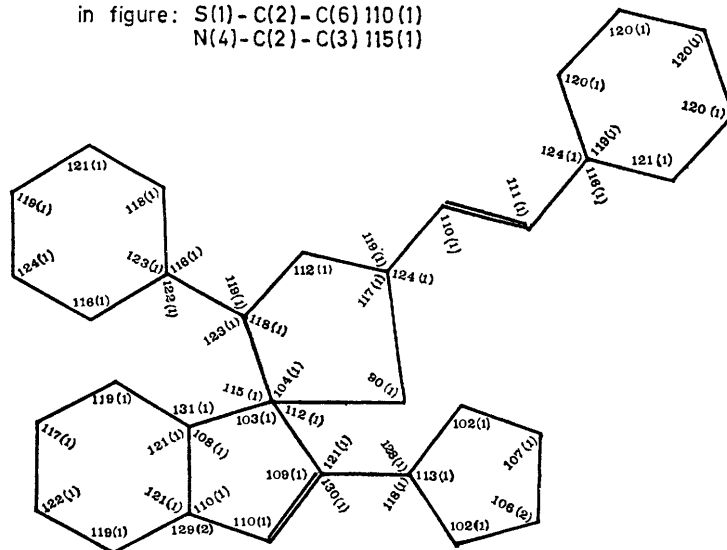


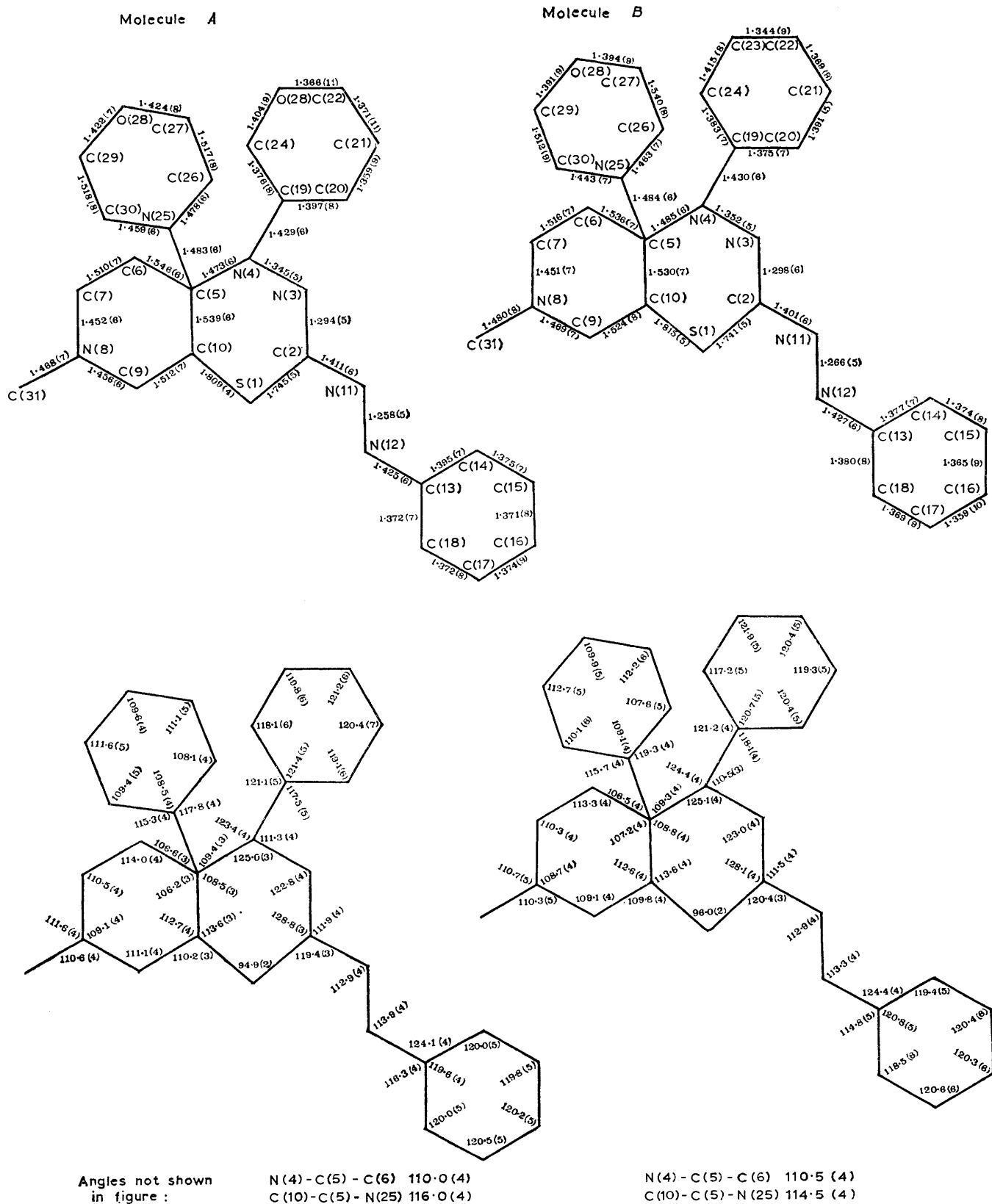
FIGURE 6 Schematic drawing of the molecule of the spiro[indene-1,3,4]thiaziazole (15a) showing the labelling of the atoms and the bond lengths (\AA) and bond angles ($^\circ$) (estimated standard deviations in parentheses)

The remaining phenyl ring, $C(41)-(46)$, is inclined by 18.9° to the plane of the thiadiazole ring; *cf.* an average of 51.0° for the corresponding dihedral angles in (3a) and (11). The rotation of this phenyl group is not as constrained as in (3a) and (11); the closest non-bonded intramolecular contact, $H(46) \cdots H(541)$, is 3.11 \AA .

The indene unit, $C(2)-(10)$, is almost planar, the maximum deviation being -0.057 \AA for the spiro-carbon atom, $C(2)$. The dihedral angle between the

by the indene unit is 4.4° . With this configuration, $H(4)$ is staggered with respect to the methylene hydrogen atoms at $C(51)$; the calculated distances $H(4) \cdots H(511)$ and $H(4) \cdots H(512)$ are 2.59 and 2.62 \AA , respectively. The difference in the bond angles $C(3)-N(5)-C(54)$ [$128(1)^\circ$] and $C(3)-N(5)-C(51)$ [$118(1)^\circ$] may be explained in terms of the proximity of the methylene hydrogen

¹⁷ L. Pauling, 'The Nature of the Chemical Bond,' 3rd edn., Oxford University Press, Oxford, 1960, p. 260.



atoms at C(54) to the thiadiazole ring; the shortest non-bonded separation, C(1) \cdots H(542), is 2.59 Å.

The pyrrolidine ring adopts the envelope conformation; the pseudorotational phase angle,¹⁸ P , is -17.2° [the torsion angle C(51)–C(52)–C(53)–C(54) is taken as ϕ_0].

The asymmetric unit of (11) contains two molecules which are chemically identical. The molecules are approximately related geometrically by a two-fold axis parallel to the unit cell y axis. A rotation matrix and translation vector to transform molecule B into molecule A are given in Table 9; the root mean square distance apart of the atoms in A and the corresponding transformed atoms in B is 0.119 or 0.061 Å, depending on whether the phenylazo-units are or are not included in the calculations. The sulphur–sulphur separation is 3.565 Å.

In (11) the thiadiazine and adjoining rings are *cis*-coupled. With the exception of the respective C(10) atoms the thiadiazine rings are almost planar, whereas the adjoining rings adopt the chair conformation. The dihedral angles between the least-squares planes defined by the atoms S(1), C(2), N(3), N(4), and C(5) and C(5), C(7), N(8), and C(10) are 73.1 and 71.7° for molecules A and B , respectively. As in (15a) there is a significant difference in the S(1)–C(2) bond length [average 1.743(7) Å] involving an sp^3 -hybridised carbon atom and the S(1)–C(10) distance [average 1.812(6) Å] involving the sp^3 -hybridised C(10).

The phenylazo-units are displaced out of the respective least-squares planes through atoms S(1), C(2), N(3), N(4), and C(5) in a similar manner to that found in (3a) except that the twist of the phenyl rings about the N(12)–C(13) bonds is in the opposite sense. The torsion angles N(3)–C(2)–N(11)–N(12), C(2)–N(11)–N(12)–C(13), and N(11)–N(12)–C(13)–C(14) are 172.9, -179.8 , and -18.0° for molecule A and 176.7, 179.3, and -6.6° for molecule B . The phenyl rings in the phenylazo-units make dihedral angles of 24.5 and 11.0° with the planes defined by S(1)–C(5) inclusive for A and B , respectively. The twist of the phenyl rings in the phenylazo-group about the N(12)–C(13) bonds is associated with the opening out of the N(12)–C(13)–C(14) bond angles [average 124.3(6)°] to give N(11) \cdots H(14) calculated non-bonded contacts of 2.49 and 2.44 Å in molecules A and B , respectively.

The S(1)–N(12) separations are 2.782 and 2.794 Å for A and B , respectively, indicating the possibility of weak interaction as found in (15a).

The phenyl rings at N(4) are planar and make dihedral angles of 51.5° in molecule A and 50.4° in molecule B with the respective planes through S(1)–C(5) inclusive. The morpholine rings adopt chair conformations and the corresponding dihedral angles for the basal planes of the chairs [defined by atoms C(26), C(27), C(29), and C(30)] are 72.7, and 71.9°. The orientations of these phenyl and morpholine rings with respect to the fused thiadiazine ring system give rise to several close hydro-

gen–hydrogen intramolecular non-bonded contacts as listed in Table 9(c).

The molecular packing for all three structures is such that there are no intermolecular separations significantly less than the sum of the respective van der Waals radii.

EXPERIMENTAL

Light petroleum refers to the fraction of b.p. 40–60°; n.m.r. spectra were determined for solutions in deuteriochloroform, electronic spectra for solutions in acetonitrile, and i.r. spectra for Nujol mulls.

Reaction of Dehydrodithizone with 1-Diethylamino-propyne.—A mixture of dehydrodithizone¹⁹ (0.4 g), 1-diethylamino-propyne (0.2 g), and chloroform (20 ml) was stirred for 16 h in an atmosphere of nitrogen and then subjected to thick-layer chromatography (GF 273; 1 mm); elution with ethyl acetate–light petroleum (3 : 17) gave orange-red 5-diethylamino-4-methyl-1-phenyl-3-phenylazopyrazole (3a) (0.3 g, 57%), m.p. 103–104° (from light petroleum), ν_{\max} 1 600, 1 570, and 1 500 cm^{-1} , τ 2.20 and 2.60 (10 H, m, 2 NPh), 6.96 (4 H, q, J 7 Hz) and 9.00 (6 H, t, J 7 Hz) (2 NEt), and 7.60 (3 H, s, Me), λ_{\max} 237, 336, and 440 sh nm, m/e 333 (M^+ , 45%), 318 (6), 304 (8), 261 (10), 155 (10), 105 (13), and 77 (100) (Found: C, 72.2; H, 7.1; N, 21.0. $\text{C}_{20}\text{H}_{23}\text{N}_5$ requires C, 72.1; H, 6.9; N, 21.0%). and a red oil, 4-diethylamino-5-methyl-1-phenyl-3-phenylazopyrazole (3b) (0.04 g, 8%), ν_{\max} 1 600, 1 560, and 1 500 cm^{-1} , τ 2.00 and 2.54 (10 H, m, 2 NPh), 6.84 (4 H, q, J 7 Hz) and 9.00 (6 H, t, J 7 Hz) (2 NEt), and 7.68 (3 H, s, Me), λ_{\max} 232, 333, and 436 sh nm, m/e 333 (M^+ , 42%), 318 (32), 241 (55), 199 (35), 118 (95), 105 (9), and 77 (100). The pyrazole (3a) (0.05 g) was dissolved in hydrochloric acid (5 ml) containing tin(II) chloride (0.5 g). The resulting solution was made alkaline (to pH 11) with sodium hydroxide and then extracted with ether (4 \times 20 ml). T.l.c. of the extract showed that it contained aniline; the other component, 3-amino-5-diethylamino-4-methyl-1-phenylpyrazole (0.01 g, 27%) separated as on air-sensitive solid on concentrating the extract; m.p. 168–170°, ν_{\max} 3 420, 3 340, 1 600, 1 550, and 1 515 cm^{-1} , τ 2.87 (5 H, m, NPh), 4.60br (2 H, disappears on adding D_2O , NH_2), 6.96 (4 H, q, J 7 Hz) and 8.98 (6 H, t, J 7 Hz) (2 NEt), and 8.13 (3 H, s, Me). The *p*-tolylsulphonyl derivative, m.p. 204–205°, was prepared in the usual way (Found: N, 14.3. $\text{C}_{21}\text{H}_{26}\text{N}_4\text{O}_2\text{S}$ requires N, 14.1%).

5-Dimethylamino-1,4-diphenyl-3-phenylazopyrazole (3c) (1.2 g, 83%), orange, m.p. 138–139° (from benzene–light petroleum), ν_{\max} 1 590, 1 495, 1 420, and 1 350 cm^{-1} , τ 2.20 (15 H, m, 3 Ph) and 7.40 (6 H, s, 2 NMe), λ_{\max} 240, 345, and 460 sh nm (Found: C, 75.3; H, 6.0; N, 18.6. $\text{C}_{23}\text{H}_{21}\text{N}_5$ requires C, 75.2; H, 5.75; N, 19.05%), was prepared as described above from dehydrodithizone (1.0 g) and 1-dimethylamino-2-phenylacetylene (0.6 g) in chloroform (50 ml) and separated by column chromatography [alumina type H; eluant ethyl acetate–light petroleum (1 : 9)].

Dimethyl 1,2-Dihydro-1,2-diphenylthiazolo[3,2-d]tetrazole-5,6-dicarboxylate (4).—A solution of dehydrodithizone (0.5 g) and dimethyl acetylenedicarboxylate (0.5 g) in toluene (40 ml) was heated under reflux for 48 h; the solvent was then removed under reduced pressure and the residue subjected to column chromatography to give the product (0.22 g, 28%), amber rods (from ethanol), m.p. 178–180° (lit.,⁶ 168–170°), ν_{\max} 1 740, 1 720, 1 590, 1 515, 1 485, 1 420,

¹⁸ C. Altona, H. J. Geisse, and C. Romers, *Tetrahedron*, 1968, **24**, 13.

¹⁹ A. M. Kiwan and H. M. N. H. Irving, *J. Chem. Soc. (B)*, 1971, 898.

1 320, 1 270, 1 235, and 1 100 cm^{-1} , τ 2.8 (10 H, m, 2 Ph), 6.0 (3 H, s, Me), and 6.1 (3 H, s, Me), m/e 396 (M^+ , 5%), 363 (19), 259 (9), 182 (7), 105 (20), and 77 (100) (Found: C, 57.4; H, 3.9; N, 14.1. Calc. for $\text{C}_{19}\text{H}_{16}\text{N}_4\text{O}_4\text{S}$: C, 57.6; H, 4.1; N, 14.15%).

Cycloaddition Reaction of Tetraphenylcyclopentadienone with Dehydrodithizone.—A mixture of dehydrodithizone (0.5 g), the ketone (0.68 g), and chloroform (40 ml) was refluxed for 40 h. Chromatography on kieselgel and elution

(13), 178 (80), 105 (23), and 77 (80) (Found: C, 78.7; H, 4.8; N, 8.6. $\text{C}_{42}\text{H}_{30}\text{N}_4\text{OS}$ requires C, 78.95; H, 4.8; N, 8.75%).

4a,5,6,7,8,8a-Hexahydro-6-methyl-8a-morpholino-1-phenyl-3-phenylazo-1H-pyrido[4,3-e][1,3,4]thiadiazine (11).—A suspension of dehydrodithizone (0.63 g) and 1,2,5,6-tetrahydro-1-methyl-4-morpholinopyridine (7) (0.453 g) in tetrahydrofuran (36 ml) was heated under reflux for 45 min; the resulting solution was cooled, filtered, and evaporated. The residual oil solidified when triturated with ethanol, giving

TABLE 1
Crystal data

Compound:	(3a)	(15a)	(11)
Formula	$\text{C}_{20}\text{H}_{23}\text{N}_5$	$\text{C}_{26}\text{H}_{25}\text{N}_5\text{S}$	$\text{C}_{26}\text{H}_{28}\text{N}_5\text{OS}$
M	333.4	437.6	472.6
Crystal system	Monoclinic	Monoclinic	Monoclinic
Cell dimensions measured at room temperature ($20 \pm 1^\circ\text{C}$)	$\begin{cases} a \\ b \\ c \end{cases} / \text{\AA}$ 9.817(4) 10.003(4) 20.326(7)	$\begin{cases} a \\ b \\ c \end{cases} / \text{\AA}$ 8.152(5) 20.771(12) 13.739(8)	$\begin{cases} a \\ b \\ c \end{cases} / \text{\AA}$ 17.536(8) 13.506(7) 19.493(9)
$\beta / ^\circ$	113.11(1)	100.42(4)	90.74(3)
$U / \text{\AA}^3$	1 836	2 281	4 616
$D_c / \text{g cm}^{-3}$	1.206	1.274	1.360
Space group	$P2_1/c$ (C_{2h}^2 No. 14)	$P2_1/c$ (No. 14)	$P2_1/n$ (alternative orientation of No. 14)
Z	4	4	8
$F(000)$	712	920	2 000
$\mu(\text{Cu-K}\alpha) / \text{cm}^{-1}$	5.9	14.1	14.7
Colour and crystal shape	orange tablets	red laths	Orange prisms

TABLE 2
Data collection

Compound:	(3a)	(15a)	(11)
Base hkl ; θ value	0,0,10; 24.3°	5,0,0; 28.7°	12,0,0; 31.8°
Number of steps for base hkl ; ω step width = 0.01°	90	70	80
Counting time per step (s)	1	4	1
Background counting time either side of base hkl peak(s)	9	14	16
Number of reference reflections	3	3	3
Number of reflections measured between reference reflections	50	30	50
Maximum variation in intensity sum of reference reflections (%)	4.4	7.6	6.7
Index and θ ranges for data collection	$\begin{cases} (a) & 0^\circ \leq \theta \leq 28^\circ; \pm h, k, \pm l \\ (b) & 28^\circ \leq \theta \leq 70^\circ; -h, k, \pm l \end{cases}$	$\begin{cases} 0^\circ \leq \theta \leq 30^\circ; \pm h, k, \pm l \\ 30^\circ \leq \theta \leq 50^\circ; h, k, \pm l \end{cases}$	$\begin{cases} 0^\circ \leq \theta \leq 23^\circ; \pm h, k, \pm l \\ 23^\circ \leq \theta \leq 55^\circ; h, k, \pm l \end{cases}$
Total number of reflections measured	4 827	3 354	6 801
Number of reflections related by symmetry	594	774	804
Residual for symmetry-related reflections	0.030	0.057	0.016
Total number of unique reflections	3 426	2 345	5 626
Number of significant reflections; $I \geq 3\sigma(I)$	1 938	1 221	4 220

TABLE 3

Structure refinement

Compound:	(3a)	(15a)	(11)
Number of reflections included in least-squares refinement	1 542	1 221	4 220
Unweighted residual prior to refinement	0.254	0.203	0.242
Coefficients used in weighting scheme for final cycle of refinement	$\begin{cases} a \\ b \\ c \\ F_{\min} \end{cases}$	$\begin{cases} 20.0 \\ 30.0 \\ 0.000\ 1 \\ 20.0 \end{cases}$	$\begin{cases} 20.0 \\ 20.0 \\ 0.004 \\ 13.0 \end{cases}$
		$\begin{cases} 50.0 \\ 0.005 \end{cases}$	$\begin{cases} 0.000\ 1 \\ 0.0005 \end{cases}$
		$\begin{cases} 0.0 \\ 0.053 \end{cases}$	$\begin{cases} 13.0 \\ 0.072 \end{cases}$
		$\begin{cases} 0.0 \\ 0.069 \end{cases}$	$\begin{cases} 0.01 \\ 0.092 \end{cases}$
Final unweighted residual	0.053	0.091	0.072
Final weighted residual $[(\sum w \Delta^2) / \sum w F_o ^2]^{1/2}$	0.069	0.093	0.092

with ether-light petroleum afforded two red adducts [0.605 g (50%) and 0.064 g (5%)]. The major product, 1,2,4a,7a-tetrahydro-1,2,4a,5,6,7a-hexaphenylcyclopenta[4,5]-thiazolo[3,2-d]tetrazol-7-one (5) or 1,2,4a,7a-tetrahydro-1,2,4a,6,7,7a-hexaphenylcyclopenta[4,5]thiazolo[3,2-d]tetrazol-5-one (6) had m.p. $166\text{--}169^\circ$ (decomp.), ν_{max} 1 715, 1 545, and 1 415 cm^{-1} , τ 1.80—3.40 (m, ArH), m/e 638 (M^+ , 5%), 610 (8), 414 (20), 398 (49), 384 (100), 356 (31), 254 (13), 182

the adduct (0.69 g, 64%), red prisms (from ethanol), m.p. 140° (decomp.) [lit.,⁶ $150\text{--}155^\circ$ (decomp.)], ν_{max} 1 595, 1 550, 1 400, and 1 110 cm^{-1} , τ 2.05—2.8 (10 H, m, 2 NPh), 6.2—8.8 (15 H, m), and 7.83 (3 H, s, NMe), m/e 436 (M^+ , 1%), 352 (3), 350 (3), 333 (5), 317 (17), 270 (14), 255 (19), 212 (19), 196 (19), 181 (22), 167 (67), 119 (19), 108 (39), 105 (19), 93 (89), 92 (89), and 77 (100) (Found: C, 63.1; H, 6.6; N, 19.4. $\text{C}_{23}\text{H}_{25}\text{N}_6\text{OS}$ requires C, 63.3; H, 6.5; N, 19.25%).

5,6-Dihydro-5-piperidino-4,6-diphenyl-2-phenylazo-4H-1,3,4-thiadiazine (12).—A mixture of dehydrodithizone

TABLE 4

Positional and thermal parameters for $C_{20}H_{23}N_5$ (3a) (estimated standard deviations, where appropriate, in parentheses)

(a) Positional parameters for non-hydrogen atoms

Atom	x/a	y/b	z/c
N(1)	-0.009 7(4)	0.487 1(3)	-0.119 0(2)
N(2)	0.137 9(4)	0.465 6(3)	-0.089 4(2)
C(3)	0.150 4(4)	0.350 6(4)	-0.054 4(2)
C(4)	0.012 5(4)	0.294 1(4)	-0.063 3(2)
C(5)	-0.089 1(4)	0.384 6(4)	-0.105 6(2)
C(11)	-0.065 7(4)	0.605 5(4)	-0.160 1(2)
C(12)	-0.018 0(5)	0.640 2(4)	-0.212 9(2)
C(13)	-0.072 4(6)	0.754 2(5)	-0.253 0(3)
C(14)	-0.172 2(6)	0.832 7(5)	-0.239 6(3)
C(15)	-0.219 7(6)	0.799 7(5)	-0.186 3(4)
C(16)	-0.165 8(6)	0.684 7(5)	-0.145 5(3)
N(3)	0.297 3(4)	0.305 7(4)	-0.019 5(2)
N(4)	0.309 8(4)	0.204 0(4)	0.018 8(2)
C(41)	0.458 2(5)	0.156 1(4)	0.053 5(2)
C(42)	0.474 0(5)	0.030 8(5)	0.083 8(2)
C(43)	0.612 3(6)	-0.027 1(5)	0.116 2(2)
C(44)	0.735 5(5)	0.042 1(6)	0.119 0(2)
C(45)	0.720 9(5)	0.168 5(6)	0.089 5(3)
C(46)	0.582 7(5)	0.226 8(5)	0.056 7(2)
C(40)	-0.020 4(5)	0.160 4(5)	-0.038 8(3)
N(5)	-0.242 4(3)	0.389 2(3)	-0.135 7(2)
C(51)	-0.313 2(5)	0.356 0(5)	-0.211 8(2)
C(52)	-0.332 7(8)	0.208 7(7)	-0.228 0(3)
C(53)	-0.322 6(5)	0.358 2(5)	-0.090 0(2)
C(54)	-0.463 7(5)	0.438 0(6)	-0.111 6(3)

(b) Anisotropic thermal parameters * ($U_{ij} \times 10^3$) for non-hydrogen atoms

Atom	U_{11}	U_{22}	U_{33}	$2U_{23}$	$2U_{31}$	$2U_{12}$
N(1)	39(2)	39(2)	41(2)	12(3)	31(3)	-4(3)
N(2)	40(2)	44(2)	47(2)	12(3)	32(3)	-7(3)
C(3)	46(3)	43(2)	44(2)	11(4)	38(4)	-6(4)
C(4)	50(2)	37(2)	43(2)	14(4)	41(4)	-4(4)
C(5)	47(2)	38(2)	39(2)	0(3)	33(3)	-16(4)
C(11)	47(2)	33(2)	42(2)	4(3)	28(4)	-15(4)
C(12)	57(3)	47(2)	52(2)	16(4)	46(4)	-4(4)
C(13)	73(3)	60(3)	60(3)	33(5)	52(5)	-10(5)
C(14)	57(3)	55(3)	89(4)	51(5)	38(6)	-4(5)
C(15)	76(4)	48(3)	120(5)	16(6)	97(7)	18(5)
C(16)	70(3)	49(3)	72(3)	11(5)	78(5)	6(5)
N(3)	45(2)	47(2)	45(2)	10(3)	31(3)	-2(3)
N(4)	45(2)	51(2)	50(2)	11(4)	38(3)	7(3)
C(41)	46(3)	53(3)	40(2)	-5(4)	31(4)	4(4)
C(42)	57(3)	51(3)	58(3)	12(4)	37(4)	8(4)
C(43)	63(3)	57(3)	58(3)	14(5)	26(5)	23(5)
C(44)	54(3)	84(4)	46(3)	-2(5)	14(4)	31(5)
C(45)	47(3)	84(4)	54(3)	-4(5)	25(4)	-10(5)
C(46)	51(3)	65(3)	48(3)	-2(4)	30(4)	0(5)
C(40)	56(3)	51(3)	70(3)	23(5)	45(5)	-12(4)
N(5)	37(2)	50(2)	37(2)	6(3)	27(3)	-8(3)
C(51)	53(3)	82(3)	45(2)	3(5)	27(4)	-19(5)
C(52)	115(5)	102(5)	82(4)	-64(7)	65(7)	-67(8)
C(53)	53(3)	65(3)	55(3)	12(5)	54(4)	-9(4)
C(54)	52(3)	91(4)	87(4)	24(6)	69(5)	14(5)

(c) Calculated hydrogen atom positions; all the hydrogen atoms were given an isotropic thermal parameter, U 0.06 Å² [the expression used was $\exp(-3\pi^2 U \sin^2 \theta / \lambda^2)$]

Atom	x/a	y/b	z/c
H(12)	0.056 0	0.583 0	-0.222 3
H(13)	-0.038 8	0.779 0	-0.291 9
H(14)	-0.211 3	0.915 2	-0.268 7
H(15)	-0.292 7	0.858 1	-0.176 8
H(16)	-0.198 9	0.660 0	-0.106 5
H(42)	0.384 4	-0.018 8	0.082 3
H(43)	0.622 7	-0.118 7	0.137 4
H(44)	0.835 9	0.000 9	0.142 5
H(45)	0.811 1	0.218 3	0.091 8

* In the form $\exp[-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{23}hkb^{*c*} + 2U_{31}hlc^{*a*} + 2U_{12}hka^{*b*})]$.

TABLE 4 (Continued)

Atom	x/a	y/b	z/c
H(46)	0.572 4	0.318 4	0.035 7
H(401)	0.074 5	0.115 4	-0.008 4
H(402)	-0.082 3	0.173 5	-0.010 2
H(403)	-0.075 4	0.103 3	-0.081 4
H(511)	-0.413 2	0.398 8	-0.231 5
H(512)	-0.251 0	0.393 7	-0.236 3
H(521)	-0.381 6	0.195 1	-0.280 9
H(522)	-0.233 7	0.164 0	-0.209 3
H(523)	-0.395 9	0.169 1	-0.204 6
H(531)	-0.347 4	0.260 8	-0.094 1
H(532)	-0.257 8	0.379 9	-0.039 2
H(541)	-0.515 8	0.415 0	-0.079 6
H(542)	-0.439 6	0.535 6	-0.107 4
H(543)	-0.529 2	0.416 5	-0.162 3

(0.25 g), β -piperidinostyrene (0.24 g), and chloroform (25 ml) was refluxed for 45 min. The solvent was removed and the residue recrystallised from aqueous methanol, giving the orange product (0.32 g, 73%), m.p. 82—84° (lit.,⁶ 115—117°), ν_{\max} 1 600, 1 555, 1 500, and 1 130 cm⁻¹, τ 2.10 (15 H, m, 3 Ph), 5.12 (1 H, d, J 3 Hz, \geq CH), 5.33 (1 H, d, J 3 Hz, \geq CH), and 7.20br (4 H) and 8.55br (6 H) (piperidino), m/e 441 (M^+ , 1%), 187 (100), 105 (19), 104 (50), and 77 (60) (Found: C, 70.4; H, 6.25; N, 15.7. $C_{26}H_{27}N_5S$ requires C, 70.7; H, 6.2; N, 15.85%). The n.m.r. spectrum was identical with one furnished by Dr. Rajagopalan.

Reactions of Dehydrodithizone with 2-Dialkylaminoindenes.

—Treatment of dehydrodithizone (0.5 g) with the appropriate enamine (14)²⁰ in chloroform, followed by evaporation and either thick-layer or column chromatography gave the following dark red 3'-phenyl-5'-phenylazospiro-[1H-indene-1,2'(3'H)-[1,3,4]thiadiazoles]: 2-pyrrolidino- (15a) (0.28 g, 34%) [from 2-pyrrolidinoindene (0.36 g) in chloroform (25 ml) for 24 h at room temperature], m.p. 166—167° (from pentane), ν_{\max} 1 595, 1 585, 1 540, 1 500, 1 310, and 1 160 cm⁻¹, τ 2.10 and 2.80 (14 H, m, ArH), 4.90 (1 H, s, =CH), and 6.62 (4 H, m) and 8.24 (4 H, m) (pyrrolidino), λ_{\max} 250, 315, and 484 nm, m/e 437 (M^+ , 29%), 436 (100), 274 (40), 215 (56), 105 (7), and 77 (45) (Found: C, 71.6; H, 5.15; N, 15.9; S, 7.4. $C_{26}H_{23}N_5S$ requires C, 71.4; H, 5.3; N, 16.0; S, 7.3%). 2-piperidino- (15b) (0.35 g, 40%) [from 2-piperidinoindene (0.41 g) in refluxing chloroform (50 ml) for 1 h], m.p. 138—140° (from pentane), ν_{\max} 1 595, 1 575, 1 540, 1 495, 1 305, and 1 155 cm⁻¹, τ 2.10 and 2.77 (14 H, m, ArH), 4.56 (1 H, s, =CH), and 6.80br (4 H) and 8.54br (6 H) (piperidino), λ_{\max} 250, 312, and 486 nm, m/e 451 (M^+ , 33%), 450 (100), 319 (12), 288 (35), 229 (35), 105 (14), and 77 (37) (Found: C, 72.0; H, 5.4; N, 15.5. $C_{27}H_{25}N_5S$ requires C, 71.8; H, 5.6; N, 15.5%). 2-morpholino- (15c) (0.35 g, 39%) [from 2-morpholinoindene (0.4 g) in chloroform (25 ml) for 48 h at room temperature], m.p. 170—171° (from pentane), ν_{\max} 1 600, 1 575, 1 540, 1 500, 1 310, 1 155, and 1 120 cm⁻¹, τ 2.10 and 2.50 (14 H, m, ArH), 4.46 (1 H, s, =CH), and 6.40 (4 H, m) and 6.80 (4 H, m) (morpholino), λ_{\max} 250, 305, and 488 nm, m/e 453 (M^+ , 30%), 452 (100), 331 (15), 290 (34), 231 (26), 105 (10), and 77 (51) (Found: C, 69.3; H, 5.4; N, 15.3. $C_{26}H_{23}N_5OS$ requires C, 68.85; H, 5.1; N, 15.45%).

Crystal Structure Determinations.—The crystal data for compounds (3a), (15a), and (11) are listed in Table 1. Preliminary unit cell parameters and space group information were obtained for all three from Weissenberg and precession photographs. In the cases of compounds (3a) and (11), crystal fragments were cut from larger crystals and mounted

²⁰ A. T. Blomquist and E. J. Moriconi, *J. Org. Chem.*, 1961, **26**, 3761.

TABLE 5

Positional and thermal parameters for $C_{26}H_{23}N_5S$ (15a) (estimated standard deviations, where appropriate, in parentheses)

(a) Positional parameters for non-hydrogen atoms			
Atom	x/a	y/b	z/c
S	0.019 6(4)	0.034 8(2)	0.474 9(2)
N(1)	0.135 7(13)	0.422 5(5)	0.638 9(8)
N(2)	0.074 8(13)	0.374 8(5)	0.677 0(8)
N(3)	0.169 9(12)	0.459 9(5)	0.486 0(7)
N(4)	0.141 4(11)	0.445 2(4)	0.389 1(7)
N(5)	0.323 4(14)	0.318 8(5)	0.349 0(9)
C(1)	0.113 5(16)	0.415 0(6)	0.538 4(11)
C(2)	0.060 7(14)	0.381 6(6)	0.358 7(8)
C(3)	0.164 7(14)	0.335 5(6)	0.306 5(8)
C(4)	0.068 5(17)	0.313 0(6)	0.223 8(10)
C(5)	-0.091 9(16)	0.342 9(7)	0.209 7(10)
C(6)	-0.099 2(18)	0.386 5(6)	0.285 5(10)
C(7)	-0.242 6(19)	0.420 8(7)	0.288 8(11)
C(8)	-0.382 1(17)	0.414 1(8)	0.209 9(14)
C(9)	-0.367 9(22)	0.369 3(8)	0.134 8(13)
C(10)	-0.225 4(19)	0.333 5(7)	0.134 9(11)
C(21)	0.109 0(16)	0.378 1(6)	0.782 8(10)
C(22)	0.213 4(18)	0.422 9(7)	0.836 1(11)
C(23)	0.243 1(18)	0.420 4(8)	0.939 9(13)
C(24)	0.154 8(24)	0.376 9(9)	0.988 6(12)
C(25)	0.050 4(23)	0.333 8(7)	0.936 0(13)
C(26)	0.025 7(17)	0.334 4(6)	0.832 1(11)
C(41)	0.209 0(16)	0.486 3(6)	0.322 5(10)
C(42)	0.156 1(14)	0.482 6(6)	0.221 8(9)
C(43)	0.230 6(17)	0.526 3(6)	0.164 4(10)
C(44)	0.345 9(17)	0.569 7(7)	0.203 1(12)
C(45)	0.398 9(19)	0.570 8(7)	0.304 3(13)
C(46)	0.329 7(17)	0.529 4(7)	0.366 5(10)
C(51)	0.408 5(20)	0.266 7(7)	0.301 8(12)
C(52)	0.576 2(23)	0.262 9(8)	0.368 9(18)
C(53)	0.557 7(21)	0.294 3(10)	0.461 1(16)
C(54)	0.425 8(18)	0.345 5(8)	0.436 3(10)

(b) Anisotropic parameters* ($U_{ij} \times 10^3$) for non-hydrogen atoms

Atom	U_{11}	U_{22}	U_{33}	$2U_{23}$	$2U_{31}$	$2U_{12}$
S	71(2)	47(2)	50(2)	-6(4)	30(3)	-25(4)
N(1)	66(7)	53(7)	49(8)	9(13)	33(11)	-7(13)
N(2)	67(8)	65(8)	47(8)	9(12)	48(12)	15(12)
N(3)	56(7)	53(7)	38(7)	-12(12)	2(11)	1(11)
N(4)	58(7)	39(6)	39(7)	-9(11)	11(11)	-25(11)
N(5)	58(8)	41(7)	84(9)	-4(12)	50(15)	7(12)
C(1)	56(9)	50(9)	65(10)	-15(15)	7(15)	19(15)
C(2)	42(8)	52(8)	46(7)	-24(12)	-25(12)	-8(13)
C(3)	54(10)	58(10)	53(9)	-6(16)	12(17)	21(16)
C(4)	63(10)	43(8)	47(9)	-5(14)	5(15)	12(15)
C(5)	49(10)	59(10)	69(10)	15(18)	-39(16)	-29(17)
C(6)	69(11)	45(9)	51(9)	-25(15)	26(16)	-47(17)
C(7)	48(9)	64(10)	85(11)	28(17)	30(17)	7(17)
C(8)	29(9)	63(10)	145(15)	67(22)	-1(20)	-19(15)
C(9)	94(14)	61(12)	92(13)	4(20)	-16(21)	-63(21)
C(10)	63(10)	74(12)	83(11)	12(18)	55(19)	4(19)
C(21)	49(8)	44(8)	78(11)	35(16)	74(16)	20(14)
C(22)	73(10)	62(10)	66(10)	19(17)	19(16)	-8(17)
C(23)	59(10)	96(12)	93(13)	0(22)	-7(18)	-3(18)
C(24)	138(17)	77(12)	70(12)	22(20)	72(24)	31(22)
C(25)	136(15)	50(11)	105(14)	24(19)	155(24)	52(20)
C(26)	93(11)	48(9)	86(11)	-15(16)	93(18)	27(16)
C(41)	53(9)	39(8)	71(11)	-23(14)	24(15)	-8(14)
C(42)	49(8)	64(10)	43(9)	-30(14)	-9(13)	-36(14)
C(43)	71(10)	51(9)	79(10)	23(16)	79(17)	-7(16)
C(44)	58(10)	60(10)	109(14)	48(18)	18(18)	-51(17)
C(45)	89(12)	66(11)	91(12)	14(18)	-9(20)	18(18)
C(46)	74(10)	60(9)	63(10)	48(17)	-5(16)	-21(17)
C(51)	69(10)	61(10)	106(13)	-30(18)	53(19)	-12(17)
C(52)	84(14)	69(13)	189(22)	-45(26)	68(29)	41(20)
C(53)	59(13)	124(17)	154(19)	47(31)	30(25)	46(23)
C(54)	62(10)	102(12)	63(10)	-26(20)	-8(16)	7(21)

* In the form $\exp[-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{23}hkb^{*c*} + 2U_{31}hlc^{*a*} + 2U_{12}hka^{*b*})]$.

TABLE 5 (Continued)

(c) Calculated hydrogen atom positions; all the hydrogen atoms were given an isotropic thermal parameter, $U = 0.10 \text{ \AA}^2$ [the expression used was $\exp(-8\pi^2U\sin^2\theta/\lambda^2)$]

Atom	x/a	y/b	z/c
H(4)	0.104 1	0.280 2	0.178 5
H(7)	-0.249 2	0.450 0	0.345 9
H(8)	-0.485 7	0.440 2	0.208 1
H(9)	-0.464 7	0.363 3	0.079 5
H(10)	-0.219 7	0.301 2	0.081 5
H(22)	0.267 8	0.456 9	0.801 1
H(23)	0.327 4	0.449 9	0.979 1
H(24)	0.169 0	0.377 7	1.062 4
H(25)	-0.009 3	0.301 5	0.970 9
H(26)	-0.053 2	0.302 8	0.793 4
H(42)	0.069 9	0.450 7	0.191 2
H(43)	0.195 4	0.524 9	0.090 9
H(44)	0.392 7	0.600 7	0.159 5
H(45)	0.488 3	0.601 8	0.333 7
H(46)	0.366 2	0.530 8	0.440 0
H(511)	0.420 1	0.278 8	0.232 9
H(512)	0.346 9	0.224 9	0.300 6
H(521)	0.662 2	0.285 7	0.338 2
H(522)	0.609 8	0.216 7	0.381 3
H(531)	0.665 8	0.314 4	0.492 7
H(532)	0.522 7	0.262 0	0.507 5
H(541)	0.475 4	0.387 8	0.421 8
H(542)	0.361 1	0.351 2	0.491 0

about the a and b axes, respectively, for use in the X-ray measurements. For (3a) the crystal fragment had dimensions $0.34 \times 0.09 \times 0.14$ mm, parallel to a , b , and c , respectively, whereas for (11) the fragment was approximately equidimensional (0.23 mm). For (15a) a lath-shaped crystal of dimensions $0.46 \times 0.02 \times 0.08$ mm was mounted about the a axis. Refined cell parameters were obtained in each case by least-squares refinement of the θ values of 20 reflections measured on a Hilger-Watts Y290 automatic four-circle diffractometer with $Cu-K\alpha_1$ radiation ($\lambda 1.540 5 \text{ \AA}$). The diffractometer is equipped with a pulse-height analyser and a scintillation counter, and intensity data were also collected on the instrument by using Ni-filtered copper radiation (see Table 2). The $\omega/2\theta$ step scanning method was used and the width of scan for each reflection as an integral number of steps was evaluated from the expression $(A + B \tan \theta)$ where A is the scan width at a θ value of zero, deduced from the θ value of the base reflection and B is a dispersion constant (0.142°) for $Cu-K\alpha$ radiation. Stationary background counts were measured for a constant fraction of the step scan time before and after each scan. Gradual variations in the experimental conditions during data collection were monitored by measuring reference reflections at constant intervals and the reflection data were scaled to these reference reflections. Symmetry-related reflections were collected over the low angle ranges (see Table 2) to check for internal consistency and weighted averages for these reflections were incorporated in the sets of independent reflections. Lorentz and polarisation corrections were applied to all reflections but no corrections were made for absorption. In the case of (3a) a set of normalised structure factors, $|E_h|$, was computed from the observed structure factors by using the K -curve method of Karle and Karle.²¹

Structure solution and refinement. The structure of (3a) was determined by using a weighted multi-solution tangent refinement²² to determine phases for 252 reflections with

²¹ J. Karle and I. L. Karle, in 'Computing Methods in Crystallography,' ed. J. S. Rollett, Pergamon, Oxford, 1965, p. 151.

²² G. Germain, P. Main, and M. M. Woolfson, *Acta Cryst.*, 1971, **27A**, 368.

TABLE 6

Positional and thermal parameters for $C_{23}H_{28}N_6OS$ (11)
(estimated standard deviations, where appropriate,
in parentheses)

(a) Positional parameters for non-hydrogen atoms			
Atom	x/a	y/b	z/c
Molecule A			
S	0.220 8(1)	0.125 0(1)	-0.076 6(1)
C(2)	0.174 3(2)	0.144 3(3)	-0.155 1(2)
N(3)	0.186 1(2)	0.101 5(3)	-0.213 5(2)
N(4)	0.240 3(2)	0.032 3(3)	-0.222 2(2)
C(5)	0.296 2(2)	0.001 4(3)	-0.169 4(2)
C(6)	0.319 7(3)	-0.107 6(3)	-0.181 3(3)
C(7)	0.256 1(3)	-0.181 1(3)	-0.170 4(3)
N(8)	0.226 5(2)	-0.172 4(3)	-0.101 4(2)
C(9)	0.195 8(3)	-0.073 2(4)	-0.092 2(3)
C(10)	0.257 5(3)	0.004 2(3)	-0.099 0(2)
N(11)	0.114 5(2)	0.213 9(3)	-0.159 4(2)
N(12)	0.096 4(2)	0.248 1(3)	-0.101 9(2)
C(13)	0.035 8(3)	0.318 4(3)	-0.104 9(2)
C(14)	0.012 8(3)	0.368 0(4)	-0.164 4(3)
C(15)	-0.044 5(3)	0.437 3(4)	-0.161 8(3)
C(16)	-0.079 1(3)	0.457 2(4)	-0.100 7(4)
C(17)	-0.056 5(4)	0.408 2(4)	-0.042 1(4)
C(18)	0.001 1(3)	0.339 5(4)	-0.043 9(3)
C(19)	0.239 1(3)	-0.005 1(3)	-0.290 7(2)
C(20)	0.169 5(4)	-0.039 3(4)	-0.317 1(3)
C(21)	0.166 1(5)	-0.073 8(5)	-0.382 6(4)
C(22)	0.230 3(6)	-0.075 5(5)	-0.421 9(3)
C(23)	0.298 8(5)	-0.042 2(5)	-0.396 9(4)
C(24)	0.304 1(3)	-0.006 1(4)	-0.329 5(3)
N(25)	0.366 5(2)	0.061 6(3)	-0.175 9(2)
C(26)	0.358 0(3)	0.166 0(3)	-0.1974 (3)
C(27)	0.436 0(3)	0.204 6(4)	-0.216 9(4)
O(28)	0.487 7(2)	0.200 7(3)	-0.160 0(2)
C(29)	0.495 1(3)	0.101 2(5)	-0.137 0(4)
C(30)	0.418 7(3)	0.057 8(4)	-0.117 1(3)
C(31)	0.167 9(4)	-0.247 3(5)	-0.088 1(4)
Molecule B			
S	0.254 4(1)	0.009 4(1)	0.085 4(1)
C(2)	0.319 4(3)	0.019 9(3)	0.153 4(3)
N(3)	0.322 2(2)	-0.031 3(3)	0.209 6(2)
N(4)	0.270 8(2)	-0.102 5(3)	0.224 7(2)
C(5)	0.202 6(3)	-0.127 7(3)	0.182 2(3)
C(6)	0.180 6(3)	-0.236 8(4)	0.192 4(3)
C(7)	0.238 2(3)	-0.308 6(4)	0.163 2(3)
N(8)	0.248 3(3)	-0.290 2(3)	0.090 5(3)
C(9)	0.280 0(3)	-0.190 4(4)	0.081 8(3)
C(10)	0.222 2(3)	-0.114 5(4)	0.106 5(3)
N(11)	0.377 7(2)	0.090 6(3)	0.151 4(2)
N(12)	0.378 7(2)	0.138 3(3)	0.095 5(2)
C(13)	0.437 3(3)	0.211 4(3)	0.093 3(3)
C(14)	0.483 7(3)	0.236 5(4)	0.148 1(3)
C(15)	0.538 7(3)	0.307 7(4)	0.139 9(3)
C(16)	0.548 1(4)	0.352 4(5)	0.077 7(4)
C(17)	0.502 3(5)	0.328 0(6)	0.023 5(4)
C(18)	0.444 7(4)	0.258 2(5)	0.030 8(3)
C(19)	0.290 1(3)	-0.149 4(3)	0.288 4(2)
C(20)	0.363 6(3)	-0.183 1(4)	0.297 5(3)
C(21)	0.386 3(3)	-0.225 9(4)	0.359 3(3)
C(22)	0.334 7(4)	-0.234 8(4)	0.411 1(3)
C(23)	0.262 5(4)	-0.203 7(5)	0.402 0(3)
C(24)	0.237 4(3)	-0.158 6(4)	0.340 2(3)
N(25)	0.136 7(2)	-0.068 0(3)	0.205 3(2)
C(26)	0.150 1(3)	0.030 2(4)	0.234 7(3)
C(27)	0.076 3(4)	0.062 7(5)	0.270 2(4)
O(28)	0.014 3(3)	0.066 7(4)	0.224 7(3)
C(29)	0.002 9(4)	-0.025 6(6)	0.194 5(5)
C(30)	0.072 8(3)	-0.063 1(5)	0.158 1(4)
C(31)	0.299 6(5)	-0.365 1(6)	0.060 3(4)

TABLE 6 (Continued)

(b) Anisotropic thermal parameters * ($U_{ij} \times 10^3$) for non-hydrogen atoms						
Atom	U_{11}	U_{22}	U_{33}	$2U_{23}$	$2U_{31}$	$2U_{12}$
Molecule A						
S	57(1)	40(1)	49(1)	-13(1)	3(1)	21(1)
C(2)	42(2)	38(2)	58(3)	-6(4)	9(4)	9(4)
N(3)	44(2)	36(2)	50(2)	-8(3)	14(3)	8(3)
N(4)	42(2)	43(2)	45(2)	-8(3)	5(3)	22(3)
C(5)	47(3)	39(2)	49(3)	5(4)	4(4)	14(4)
C(6)	59(3)	39(2)	64(3)	-2(4)	14(5)	19(4)
C(7)	74(3)	39(3)	66(3)	-8(4)	7(5)	3(5)
N(8)	69(3)	39(2)	66(3)	10(4)	16(4)	-20(4)
C(9)	60(3)	50(3)	60(3)	1(5)	20(5)	-15(5)
C(10)	52(3)	38(2)	52(3)	-7(4)	2(4)	12(4)
N(11)	47(2)	35(2)	56(2)	-14(3)	6(4)	15(3)
N(12)	46(2)	37(2)	61(3)	-10(4)	18(4)	13(3)
C(13)	46(3)	36(2)	63(3)	-12(4)	15(4)	5(4)
C(14)	60(3)	51(3)	69(3)	-3(5)	13(5)	9(5)
C(15)	64(3)	50(3)	93(4)	6(6)	1(6)	21(5)
C(16)	57(3)	48(3)	118(5)	-18(7)	26(7)	30(5)
C(17)	86(4)	61(4)	97(4)	-25(7)	56(7)	39(6)
C(18)	73(3)	57(3)	77(4)	-14(5)	35(6)	40(5)
C(19)	67(3)	41(3)	50(3)	2(4)	2(5)	27(5)
C(20)	89(4)	51(3)	69(4)	-24(6)	-21(6)	25(6)
C(21)	123(6)	75(4)	82(5)	-48(7)	-65(9)	60(8)
C(22)	178(8)	71(4)	60(4)	-25(6)	-11(10)	94(10)
C(23)	131(4)	64(4)	69(4)	16(6)	67(8)	94(7)
C(24)	91(4)	59(3)	62(3)	18(5)	49(6)	63(6)
N(25)	42(2)	41(2)	67(2)	9(4)	8(4)	6(3)
C(26)	58(3)	42(3)	95(4)	31(5)	21(5)	-8(5)
C(27)	63(3)	64(3)	117(5)	26(6)	15(7)	-22(5)
O(28)	64(2)	71(3)	136(4)	24(5)	-8(5)	-40(4)
C(29)	52(3)	77(4)	128(5)	24(7)	-14(6)	-13(6)
C(30)	55(3)	60(3)	85(4)	6(6)	-21(5)	-4(5)
C(31)	126(5)	60(4)	97(4)	3(6)	49(8)	-73(7)
Molecule B						
S	74(1)	55(1)	64(1)	30(1)	-27(1)	-26(1)
C(2)	48(3)	44(3)	63(3)	10(5)	10(4)	-2(4)
N(3)	44(2)	43(2)	61(2)	12(4)	5(4)	-12(3)
N(4)	47(2)	41(2)	55(2)	10(3)	4(3)	-14(3)
C(5)	54(3)	44(3)	66(3)	-4(4)	-12(5)	-6(4)
C(6)	54(3)	49(3)	76(3)	-5(5)	0(5)	-29(4)
C(7)	76(3)	45(3)	80(4)	-6(5)	0(6)	-5(5)
N(8)	79(3)	59(3)	84(3)	-31(5)	13(5)	-11(5)
C(9)	70(3)	63(3)	83(4)	-9(6)	19(6)	-10(6)
C(10)	65(3)	62(3)	71(3)	13(5)	-11(5)	-32(5)
N(11)	55(2)	41(2)	65(3)	16(4)	8(4)	-4(4)
N(12)	60(2)	40(2)	66(3)	18(4)	14(4)	-10(4)
C(13)	62(3)	42(3)	70(3)	9(5)	19(5)	-1(5)
C(14)	66(3)	58(3)	83(4)	19(5)	-3(6)	-8(5)
C(15)	79(4)	65(4)	97(4)	-15(7)	15(7)	-19(6)
C(16)	96(5)	83(5)	119(6)	-10(8)	31(9)	-74(7)
C(17)	142(6)	100(5)	101(5)	40(8)	25(10)	-117(10)
C(18)	97(4)	83(4)	83(4)	17(7)	18(7)	-66(7)
C(19)	57(3)	39(2)	55(3)	3(4)	13(5)	-23(4)
C(20)	60(3)	48(3)	66(3)	11(5)	-9(5)	-9(5)
C(21)	82(4)	56(3)	77(4)	27(6)	-25(7)	-16(6)
C(22)	100(4)	65(4)	75(4)	30(6)	-38(7)	-69(6)
C(23)	118(5)	79(4)	51(3)	-4(6)	28(7)	-90(7)
C(24)	80(4)	61(3)	62(3)	-8(5)	31(5)	-27(5)
N(25)	54(2)	45(2)	102(3)	-25(4)	4(4)	-3(4)
C(26)	63(3)	57(3)	127(5)	-33(6)	14(6)	7(5)
C(27)	85(5)	64(4)	168(6)	-41(8)	62(9)	11(7)
O(28)	59(3)	82(3)	218(5)	-33(6)	5(6)	17(5)
C(29)	64(4)	78(5)	205(8)	-26(9)	-12(9)	8(7)
C(30)	52(3)	68(4)	144(5)	-19(7)	-24(7)	44(5)
C(31)	123(6)	88(5)	132(6)	-71(9)	60(10)	12(9)

* In the form $\exp[-2\pi^2(U_{11}h^2a^{*2} + U_{22}h^2b^{*2} + U_{33}h^2c^{*2} + 2U_{23}h^2b^*c^* + 2U_{31}hc^*a^* + 2U_{12}hka^*b^*)]$.

TABLE 6 (Continued)

(c) Calculated hydrogen atom positions; all hydrogen atoms were assigned an isotropic thermal parameter $U = 0.10 \text{ \AA}^2$ in the expression $\exp(-8\pi^2 U \sin^2 \theta / \lambda^2)$.

Atom †	x/a	y/b	z/c
Molecule A			
H(61)	0.362 3	-0.123 8	-0.148 0
H(62)	0.338 2	-0.114 8	-0.229 0
H(71)	0.278 2	-0.249 3	-0.176 5
H(72)	0.216 0	-0.168 9	-0.205 3
H(91)	0.171 9	-0.068 0	-0.046 4
H(92)	0.155 9	-0.060 4	-0.128 9
H(10)	0.297 3	-0.012 0	-0.062 9
H(14)	0.038 6	0.353 3	-0.208 8
H(15)	-0.061 0	0.472 9	-0.205 0
H(16)	-0.122 3	0.506 3	-0.098 5
H(17)	-0.082 2	0.425 4	0.002 4
H(18)	0.018 1	0.304 0	-0.000 2
H(20)	0.123 6	-0.038 9	-0.286 3
H(21)	0.116 2	-0.100 2	-0.403 1
H(22)	0.228 0	-0.099 5	-0.469 4
H(23)	0.343 0	-0.044 9	-0.428 3
H(24)	0.354 8	0.015 8	-0.309 2
H(261)	0.338 0	0.205 7	-0.157 9
H(262)	0.321 6	0.170 0	-0.236 7
H(271)	0.430 2	0.275 8	-0.232 9
H(272)	0.455 6	0.164 7	-0.256 4
H(291)	0.530 0	0.100 0	-0.094 8
H(292)	0.518 7	0.059 4	-0.173 2
H(301)	0.396 4	0.094 7	-0.078 0
H(302)	0.425 1	-0.014 3	-0.103 2
H(311)	0.147 3	-0.238 6	-0.014 4
H(312)	0.125 0	-0.239 6	-0.122 9
H(313)	0.190 8	-0.314 3	-0.093 2

Molecule B			
H(61)	0.129 9	-0.248 8	0.168 3
H(62)	0.174 5	-0.251 1	0.242 3
H(71)	0.218 9	-0.379 0	0.169 3
H(72)	0.287 6	-0.301 6	0.188 4
H(91)	0.292 9	-0.179 7	0.032 4
H(92)	0.328 8	-0.184 1	0.110 1
H(10)	0.173 4	-0.125 5	0.078 6
H(14)	0.475 2	0.203 9	0.194 3
H(15)	0.571 6	0.328 6	0.179 8
H(16)	0.589 5	0.402 7	0.069 9
H(17)	0.511 7	0.359 7	-0.022 9
H(18)	0.407 6	0.243 1	-0.007 4
H(20)	0.400 9	-0.176 5	0.259 0
H(21)	0.440 8	-0.251 3	0.366 8
H(22)	0.348 6	-0.264 2	0.456 3
H(23)	0.224 7	-0.212 2	0.439 3
H(24)	0.182 6	-0.135 1	0.333 0
H(261)	0.163 7	0.080 1	0.198 3
H(262)	0.193 9	0.028 8	0.269 5
H(271)	0.083 5	0.128 5	0.292 8
H(272)	0.063 9	0.012 1	0.306 9
H(291)	-0.041 5	-0.023 6	0.162 4
H(292)	-0.008 9	-0.076 9	0.232 1
H(301)	0.084 6	-0.013 9	0.119 5
H(302)	0.063 1	-0.128 9	0.136 3
H(311)	0.306 5	-0.350 5	0.009 6
H(312)	0.351 0	-0.364 0	0.083 1
H(313)	0.277 1	-0.433 1	0.064 4

† For atoms H(61)–(92) and H(261)–(313) the first digit, or first two digits if there are more than two, refer to the atom to which the hydrogen is bonded.

TABLE 7

Molecular geometry for $C_{20}H_{23}N_5$ (3a)

Least-squares planes through the atomic positions and, in parentheses, distances of the atoms from the planes (Å). X , Y , and Z refer to orthogonal co-ordinates (Å), obtained by the transformation:

$$\begin{bmatrix} X \\ Y \\ Z \end{bmatrix} = \begin{bmatrix} a \sin \beta & 0 & 0 \\ 0 & b & 0 \\ a \cos \beta & 0 & c \end{bmatrix} \begin{bmatrix} x/a \\ y/b \\ z/c \end{bmatrix}$$

Plane (i): N(1), N(2), C(3), C(4), and C(5)

$$0.036 7X + 0.485 6Y + 0.873 4Z - 0.270 2 = 0$$

$$[N(1) 0.013, N(2) -0.015, C(3) 0.010, C(4) -0.002, C(5) -0.007, C(11) 0.028, N(3) -0.034, N(4) 0.115, C(41) 0.047, C(40) -0.117, N(5) -0.054]$$

Plane (ii): C(11), C(12), C(13), C(14), C(15), and C(16)

$$0.751 3X + 0.528 8Y + 0.394 9Z - 1.577 9 = 0$$

$$[C(11) -0.006, C(12) 0.005, C(13) -0.001, C(14) -0.002, C(15) 0.001, C(16) 0.003, N(1) -0.007]$$

Plane (iii): C(41), C(42), C(43), C(44), C(45), and C(46)

$$0.089 6X + 0.403 6Y + 0.910 6Z - 0.389 6 = 0$$

$$[C(41) -0.006, C(42) 0.006, C(43) -0.002, C(44) -0.002, C(45) 0.001, C(46) 0.003, N(3) -0.319, N(4) -0.054]$$

Dihedral angles between planes:

$$\begin{array}{ll} \text{(i) and (ii)} & 51.0^\circ \\ \text{(i) and (iii)} & 6.0^\circ \end{array}$$

TABLE 8

Molecular geometry for $C_{26}H_{23}N_5S$ (15a)

(a) Least-squares planes through the atomic positions and, in parentheses, distances of the atoms from the planes (Å). X , Y , and Z refer to orthogonal co-ordinates (Å) obtained by the transformation:

$$\begin{bmatrix} X \\ Y \\ Z \end{bmatrix} = \begin{bmatrix} a \sin \beta & 0 & 0 \\ 0 & b & 0 \\ a \cos \beta & 0 & c \end{bmatrix} \begin{bmatrix} x/a \\ y/b \\ z/c \end{bmatrix}$$

Plane (i): S, C(1), N(3), N(4), and C(2)

$$0.890 2X - 0.454 5Y - 0.030 8Z = -3.323 2$$

$$[S -0.010, C(1) 0.003, N(3) 0.008, N(4) -0.017, C(2) 0.015, N(1) 0.050, N(2) 0.045, C(41) 0.110]$$

Plane (ii): C(2)–(10)

$$0.345 3X + 0.734 8Y - 0.583 8Z = 3.207 3$$

$$[C(2) -0.057, C(3) 0.037, C(4) 0.011, C(5) -0.005, C(6) 0.026, C(7) -0.001, C(8) 0.025, C(9) -0.003, C(10) -0.032, N(5) 0.018]$$

Plane (iii): C(21)–(26)

$$0.753 2X - 0.647 7Y - 0.115 0Z = -5.643 6$$

$$[C(21) 0.011, C(22) -0.026, C(23) 0.027, C(24) -0.014, C(25) -0.001, C(26) 0.002, N(2) 0.010, N(1) -0.191]$$

Plane (iv): C(41)–(46)

$$0.713 3X - 0.671 2Y - 0.201 7Z = -6.388 7$$

$$[C(41) -0.007, C(42) 0.005, C(43) 0.004, C(44) -0.012, C(45) 0.011, C(46) -0.001, N(4) -0.027]$$

Dihedral angles between normals to planes (°)

$$\begin{array}{ll} \text{(i) and (ii)} & 90.5 \\ \text{(i) and (iii)} & 14.4 \\ \text{(i) and (iv)} & 18.9 \end{array}$$

(b) Dihedral angles (°) for the pyrrolidine ring

$$\begin{array}{ll} N(5)-C(51)-C(52)-C(53) & 18.0 \\ C(51)-C(52)-C(53)-C(54) & -29.9 \\ C(52)-C(53)-C(54)-N(5) & 28.7 \\ C(53)-C(54)-N(5)-C(51) & -17.5 \\ C(54)-N(5)-C(51)-C(52) & 0.3 \end{array}$$

TABLE 9

Molecular geometry for C₂₃H₂₈N₆O₈ (11)

(a) Least-squares planes defined by atomic positions and, in parentheses, distances of atoms (Å) from these planes. X, Y, and Z refer to orthogonal co-ordinates obtained by the transformation:

$$\begin{bmatrix} X \\ Y \\ Z \end{bmatrix} = \begin{bmatrix} a \sin \beta & 0 & 0 \\ 0 & b & 0 \\ -a \cos \beta & 0 & c \end{bmatrix} \begin{bmatrix} x/a \\ y/b \\ z/c \end{bmatrix}$$

Molecule A

Plane (i): S(1), C(2), N(3), N(4), and C(5)

$$0.631 \ 9X + 0.735 \ 9Y - 0.243 \ 2Z = 4.086 \ 3$$

$$[S(1) - 0.022, C(2) \ 0.024, N(3) \ 0.006, N(4) - 0.037, C(5) \ 0.029, C(10) - 0.707, N(11) \ 0.071, N(12) - 0.065]$$

Plane (ii): C(5), C(10), C(7), and N(8)

$$0.885 \ 3X - 0.232 \ 6Y + 0.402 \ 7Z = 3.211 \ 1$$

$$[C(5) \ 0.026, C(10) - 0.027, C(7) - 0.028, N(8) \ 0.029, C(6) \ 0.637, C(9) - 0.683, C(31) - 0.536]$$

Plane (iii): C(13), C(14), C(15), C(16), C(17), and C(18)

$$0.674 \ 7X + 0.716 \ 2Y + 0.178 \ 5Z = 3.139 \ 6$$

$$[C(13) - 0.002, C(14) - 0.001, C(15) \ 0.002, C(16) \ 0.000, C(17) - 0.003, C(18) \ 0.005, N(11) - 0.275, N(12) \ 0.042]$$

Plane (iv): C(19), C(20), C(21), C(22), C(23), and C(24)

$$0.212 \ 5X - 0.920 \ 3Y + 0.328 \ 6Z = -0.924 \ 8$$

$$[C(19) \ 0.000, C(20) \ 0.001, C(21) - 0.002, C(22) \ 0.002, C(23) - 0.001, C(24) \ 0.001, N(4) - 0.022]$$

Plane (v): C(26), C(27), C(29), and C(30)

$$0.079 \ 5X - 0.704 \ 9Y - 0.704 \ 9Z = 1.699 \ 3$$

$$[C(26) - 0.011, C(27) \ 0.011, C(29) - 0.011, C(30) \ 0.011, N(25) \ 0.701, O(28) - 0.654, C(5) \ 1.076]$$

Molecule B

Plane (vi): S(1), C(2), N(3), N(4), and C(5)

$$0.555 \ 8X - 0.701 \ 6Y - 0.445 \ 9Z = 1.650 \ 0$$

$$[S(1) \ 0.023, C(2) - 0.027, N(3) - 0.003, N(4) \ 0.035, C(5) - 0.029, C(10) \ 0.698, N(11) - 0.105, N(12) - 0.062]$$

Plane (vii): C(5), C(10), C(7), and N(8)

$$0.961 \ 5X + 0.187 \ 1Y + 0.201 \ 1Z = 3.830 \ 9$$

$$[C(5) - 0.032, C(10) \ 0.034, C(7) \ 0.034, N(8) - 0.035, C(6) - 0.639, C(9) \ 0.716, C(31) \ 0.520]$$

Plane (viii): C(13), C(14), C(15), C(16), C(17), and C(18)

$$0.646 \ 5X - 0.710 \ 7Y - 0.277 \ 6Z = 2.440 \ 4$$

$$[C(13) \ 0.011, C(14) \ 0.002, C(15) - 0.010, C(16) \ 0.004, C(17) \ 0.009, C(18) - 0.016, N(11) \ 0.177, N(12) \ 0.031]$$

Plane (ix): C(19), C(20), C(21), C(22), C(23), and C(24)

$$0.266 \ 3X + 0.898 \ 5Y + 0.348 \ 9Z = 1.475 \ 6$$

$$[C(19) \ 0.004, C(20) - 0.006, C(21) \ 0.000, C(22) \ 0.007, C(23) - 0.009, C(24) \ 0.003, N(4) \ 0.051]$$

Plane (x): C(26), C(27), C(29), and C(30)

$$0.053 \ 1X - 0.789 \ 1Y + 0.612 \ 0Z = 2.605 \ 4$$

$$[C(26) - 0.010, C(27) \ 0.010, C(29) - 0.010, C(30) \ 0.010, N(25) \ 0.677, O(28) - 0.624, C(5) \ 1.090]$$

Dihedral angles between normals to planes (°)

(i) and (ii)	73.1	(vi) and (vii)	71.7
(i) and (iii)	24.5	(vi) and (viii)	11.0
(i) and (iv)	51.5	(vi) and (ix)	50.4
(i) and (v)	72.7	(vi) and (x)	71.9
(i) and (vi)	93.3		

(b) Rotation matrix and translation vector to transpose molecule A into molecule B; the phenyl rings involving atoms C(13)—(18) were not included in the calculation

$$\begin{bmatrix} -0.9731 & -0.0150 & 0.2301 \\ 0.0072 & 0.9954 & 0.0956 \\ -0.2304 & 0.0947 & -0.9685 \end{bmatrix} \begin{bmatrix} 0.5601 \\ 1.7824 \\ -7.9261 \end{bmatrix}$$

TABLE 9 (Continued)

(c) Close intra-molecular non-bonded hydrogen-hydrogen contacts (Å)

	Molecule A	Molecule B
H(61) ··· H(302)	2.04	2.09
H(10) ··· H(61)	2.53	2.54
H(10) ··· H(301)	2.28	2.32
H(10) ··· H(302)	2.38	2.25
H(20) ··· H(72)	2.85	2.93
H(24) ··· H(62)	2.38	2.37
H(24) ··· H(262)	2.59	2.54
H(24) ··· H(272)	2.86	2.92

$|E_h| > 1.80$. The origin defining reflections and three others in the starting set were as follows:

<i>h</i>	<i>k</i>	<i>l</i>	$ E_h $	Phase
1	3	19	4.61	+
3	4	16	3.41	+
3	6	21	3.10	+
9	1	9	3.60	+, -
5	8	9	3.52	+, -
4	9	2	3.40	+, -

The solution with phases -, +, and + gave the highest figure of merit (1.26)²² and an *E*-map computed with this phase set revealed all the non-hydrogen atoms in the structure.

In the structure analyses of compounds (15a) and (11) the respective sulphur atoms were located from three-dimensional Patterson syntheses computed with coefficients sharpened by multiplying the observed structure factors by the function, $1/\exp(-8\pi^2 U \sin^2 \theta / \lambda^2)$, where *U*, an overall isotropic thermal parameter, was arbitrarily assessed as 0.03 Å². Initial sets of phases were computed from the sulphur atom positions and the positions of the remaining non-hydrogen atoms were determined by using the iterative weighted Fourier synthesis technique.²³

All three structures were refined by a full-matrix least-squares technique (Table 3). Initially refinement was carried out with all the non-hydrogen atoms treated isotropically. Attempts were then made to locate hydrogen atoms from difference Fourier syntheses. In the cases of (3a) and (11) most of the hydrogen atoms were detectable as diffuse electron density peaks, 0.2–0.6 e Å⁻³, but for (15a) the data were not of sufficient quality to permit the unequivocal location of any of the hydrogen atoms. In subsequent calculations, for all three compounds, hydrogen atoms were placed in calculated positions by assuming a carbon–hydrogen bond length of 1.0 Å, but no attempts were made to refine their positional or thermal parameters. Further refinement was carried out with the non-hydrogen atoms treated anisotropically. For (15a) and (11), in order to conserve computing time, a partial full-matrix technique was used in which no more than 25 atoms (225 parameters) were permitted to vary in any one cycle, although an overall scale factor was always refined. Refinement was continued until all positional parameter shifts were less than the corresponding estimated standard deviations; for (3a) and (15) this condition was also satisfied for the anisotropic thermal parameters.

Weights were assigned to the unscaled observed structure factors throughout the refinements according to a function of the type $w = d$ for $|F_o| \leq F_{\min}$, otherwise $w = [1 - \exp(-a \sin^2 \theta / \lambda^2)] / (b + |F_o| + c|F_o|^2)$. Values of the coefficients used in the final refinement cycles together with the final weighted and unweighted residuals are given in

²³ G. A. Sim, *Acta Cryst.*, 1959, **12**, 813.

Table 3. For each of the structures an analysis of the respective weighting scheme in terms of batches of increasing $\sin\theta/\lambda$ and $|F_o|$ showed a constancy in the values of $\Sigma w\Delta^2/n$.

Difference Fourier syntheses computed after the final refinement cycles showed no significant details and similarly structure factor calculations for the insignificant reflections showed no outstanding discrepancies.

The atomic scattering factors listed by Hanson *et al.*²⁴ were used in all the structure factor calculations and all computations were performed on the CDC 6600 computer at the University of London Computer Centre.

The final atomic co-ordinates and thermal parameters

† For details of Supplementary Publications see Notice to Authors No. 7, *J.C.S. Perkin I*, 1975, Index issue.

are given in Tables 4—6. Satisfactory tensor analyses of the anisotropic thermal vibration parameters were obtained in all cases.

The lists of observed and calculated structure factors are contained in Supplementary Publication No. SUP 21770 (49 pp., 1 microfiche).†

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²⁴ H. P. Hanson, F. Herman, J. D. Lea, and S. Skillman, *Acta Cryst.*, 1964, **17**, 1040.